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PART C
Liquid and Solid Waste Research

NOVEMBER 30 &
DECEMBER 1, 1987

ROYAL YORK HOTEL
TORONTO, ONTARIO, CANADA

**HAZARDOUS CONTAMINANTS
COORDINATION BRANCH
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PROCEEDINGS

TECHNOLOGY TRANSFER CONFERENCE

NOVEMBER 30 - DECEMBER 1, 1987

ROYAL YORK HOTEL

PART C

LIQUID AND SOLID WASTE RESEARCH

**Organized through the
RESEARCH ADVISORY COMMITTEE**

**Sponsored by
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INTRODUCTION

Environment Ontario holds its annual Technology Transfer Conference to report and publicize the progress made on Ministry-funded projects. These studies are carried out in Ontario universities and by private research organizations and companies.

The papers presented at the 1987 Technology Transfer Conference are included in five volumes of Conference Proceedings corresponding to the following sessions:

- Part A: Air Quality Research
- Part B: Water Quality Research
- Part C: Liquid & Solid Waste Research
- Part D: Analytical Methods
- Part E: Environmental Economics.

This part is a compilation of papers presented during Session C of the Conference.

For further information on any of the papers, the reader is kindly referred to the authors or to the Research Management Office at (416) 323-4574, 332-4573.

ACKNOWLEDGMENTS

The Conference Committee would like to thank the authors for their valuable contributions to environmental research in Ontario.

DISCLAIMER

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SESSION C: LIQUID AND SOLID WASTE RESEARCH

C1 WASTE REDUCTION STRATEGIES FOR CALIFORNIA'S PRINTED CIRCUIT BOARD INDUSTRY: RESULTS OF A STUDY AND TECHNOLOGY DEMONSTRATION PROJECT, AND POTENTIAL APPLICATION TO ONTARIO'S HEAVY METAL GENERATING INDUSTRIES.

B. Fleet, University of Toronto
C. Small, SCADA Systems, Toronto,
R. Judd, CAL-Tech Management
Associates., Sacramento, G.A. Davis,
University of Tennessee, B. Piasecki,
Clarkson University and M. Mueller,
Clarkson University, Potsdam N.Y.,
SCADA Systems Inc., Rexdale, Ontario.

C2 EXPERIMENTS ON THE MOVEMENT OF IMMISCIBLE LIQUIDS AND THEIR VAPOURS IN SOIL.

G. Farquhar, W. Abbott, R. Kell, E. McBean,
and B. Stickney, University of Waterloo,
Waterloo, Ontario.

C3 HAZARDOUS ORGANIC CHEMICALS IN GROUNDWATER AT ONTARIO LANDFILLS.

J. F. Barker, J.A. Cherry, D.A. Carey
and M.E. Muttes, University of
Waterloo, Waterloo, Ontario.

C4 NATURE OF SUBSTRATES IN INDUSTRIAL WASTES RELATIVE TO ELEMENTAL LEACHABILITY: SEQUENTIAL EXTRACTIONS AND ELUTIONS.

J.R. Kramer, J. Gleed, O. Mudroch,
P. Brassard and P. Collins, McMaster
University, Hamilton, Ontario.

C5 REPORT ON CODISPOSAL OF MUNICIPAL AND SOLID INDUSTRIAL WASTES.
D. Kirk and S. Pirani, University of Toronto, Toronto, Ontario.

C6 TECHNICAL AND ECONOMIC ASSESSMENT OF REVERSE OSMOSIS FOR THE TREATMENT OF LANDFILL LEACHATES.
T.A. Krug and S. McDougall, ZENON Environmental Inc., Burlington, Ontario.

C7 ENHANCED SANITARY LANDFILL: A DEMONSTRATION TRIAL.
G. Vicevic, B. Forrestal, A. Stevenson, Ontario Research Foundation, Mississauga, A. Martin, R.V. Anderson Associates, Ltd., Toronto, R. Rothfuss, Region of Peel, Brampton and M. McKim, CMS Rotordisk, Mississauga, Ontario.

C8 SEWAGE SLUDGE COMPOST AS TURF FERTILIZER.
J. Eggens, University of Guelph, Guelph, Ontario.

C9 DISPERSION OF THE STOUFFVILLE CONTAMINANT PLUME.
I. Proulx, R.N. Farvolden, and E.O Frind, University of Waterloo, Waterloo, Ontario.

C10 THE ECONOMIC BENEFITS OF PREVENTING GROUNDWATER CONTAMINATION.
J. Hoehn and D. Walker, Michigan State University, Lansing, Michigan.

C11 ASSESSMENT OF OVERLAND FLOW BIOLOGICAL TREATMENT TECHNOLOGY FOR REMOVAL OF ORGANIC COMPOUNDS FROM GROUNDWATER.
R. Woeller and D. Cook, Environment Ontario, Toronto, Ontario, D. Cook, Water & Earth Sciences Assoc., Carp, Ontario.

C12 OPTIMAL RECOVERY OF LEACHATE UNDER SANITARY LANDFILLS.
J.W. Molson, E.O. Frind and R.N. Farvolden, University of Waterloo, Waterloo, Ontario.

C13 EFFECTS OF INCREASING AMOUNTS OF NON-POLAR ORGANIC LIQUIDS IN DOMESTIC WASTE LEACHATE ON THE HYDRAULIC CONDUCTIVITY OF CLAY LINERS IN SOUTHWESTERN ONTARIO.
R.M. Quigley and F. Fernandez, University of Western Ontario, London, Ontario.

C14 EVALUATION OF CONTAMINANT VELOCITY IN LOW-PERMEABILITY FRACTURED SHALE.
G. Thomson, R. Blackport J. Cherry, and E. Sudicky, Institute of Groundwater, University of Waterloo, Waterloo, Ontario.

C15 ORIGIN AND STATE OF NEAR SURFACE FRACTURES IN THE CLAY TILLS OF SOUTHWESTERN ONTARIO.
M.B. Dusseault, University of Waterloo, Waterloo, Ontario.

C16 **WASTE MANAGEMENT PLANNING FOR PHARMACEUTICAL INDUSTRY: PHASE II DATA ANALYSIS AND ASSESSMENT.**
R.A. Stairs and R.C. Makhija, Trent University, Peterborough, Ontario.

C17 **MUNICIPAL SOLID WASTE FEASIBILITY OF GASIFICATION WITH PLASMA ARC.**
G.W. Carter and A. Tsangaris,
Resorption Canada Ltd., Ottawa, Ontario.

C18 **DEVELOPMENT OF GUIDELINES FOR THE UTILIZATION OF INDUSTRIAL WASTES IN BACKFILL AND CONSTRUCTION APPLICATIONS IN ONTARIO.**
M. Kelleher, G. Zukovs, and S. Dedhar, CANVIRO Consultants, Mississauga, Ontario.

CP1 **SLOW RATE INFILTRATION LAND TREATMENT AND RECIRCULATION OF LANDFILL LEACHATE IN ONTARIO.**
R.A. McBride, A.M. Gordon and P.H. Groenevelt, Departments of Land Resource Science and Environmental Biology, University of Guelph, Guelph, Ontario.

CP2 **SAMPLING GROUNDWATERS FOR VOLATILE ORGANIC CONTAMINANTS.**
J.F. Barker, T.A. McAlary and G.M. Travis, Institute for Groundwater Research, University of Waterloo, Waterloo, Ontario.

Waste Reduction Strategies
for California's Printed Circuit Board Industry;
Results of a Study and Technology Demonstration Project, and
Potential Application to Ontario's Heavy Metal Generating Industries.

B.Fleet^{1,2}, R.L.Judd³, C.E.Small², G.A.Davis⁴, B.Piasecki⁵,
M.J.Mueller⁵, B.Cardoza² and J.Kassirer².

Overview of Project

This project (Judd et al, 1986), sponsored by the State of California, Department of Health Services had several objectives;

- * To prepare an interim report giving a general evaluation of the feasibility for waste reduction in California's printed circuit board industry
- * To focus on alternatives to land disposal of the industry's hazardous wastes, specifically zero-sludge waste management strategies utilizing resource recycling technologies
- * To carry out three case studies for three circuit board plants of varying size and type of business, to evaluate the feasibility of the above waste reduction strategies
- * To submit a final report that relates the general evaluation with the case studies and technology review, and presents conclusions on the need and feasibility of these waste reduction strategies

Pressures to Move Beyond Sludge Disposal

The Resource Conservation and Recovery Act has had a variable but generally strong impact in different U.S. states. In California, which leads the way in terms of environmental law enforcement, the results have been evidenced by;

- * A strong opposition to continued land disposal of hazardous wastes, with several waste categories being banned from disposal
- * A restricted number of available chemical landfill sites, with the

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residual sites becoming more selective regarding the types and amounts of acceptable wastes

- * Increasing costs of heavy metal sludge disposal, with rates currently ranging from \$100-600 (U.S.) per ton

As a result of this situation many printed circuit board companies are now actively evaluating their future waste management options.

Industry Survey

A survey of the circuit board industry was first carried out in order to try and define current waste management practices, and to review manufacturing and waste generation procedures as well as the industry's attitudes towards new environmental regulations. When the survey was started the industry was just beginning to emerge from the depths of a major economic recession and waste management problems, particularly investment in new plant to meet stricter environmental controls, was not the major concern for many companies.

As a result of this recession there seems to have been some moves towards;

- * a restructuring of the industry involving a consolidation/regrouping
- * increased specialization in higher value-added products (multilayer boards, flexible circuits, etc.)
- * a greater dependence on process control and automation to improve productivity and product quality

Moreover, during the time that data was being collected for the study, from mid-1986 until October 1987, there was strong evidence of a slow but steady economic improvement in the electronics industry.

Technologies for Waste Reduction and Recycling

A major section of the study reviewed waste minimization strategies as well as the current status of technologies for recovery and recycling of heavy metal hazardous wastes. Industry attitudes towards in-plant changes and process modifications to provide either less toxic or more easily treatable chemistries were also examined. Recycling/recovery waste treatment technologies reviewed briefly included: ion-exchange, electrolytic recovery, membrane separation processes including reverse osmosis, electrodialysis and Donnan dialysis-coupled transport. Ultrafiltration, cross-flow microfiltration, evaporative and biotechnology processes were also covered.

Zero-Sludge Waste Management Strategies

In the area of waste management strategies a zero-sludge heavy metal hazardous waste management system was reviewed and the performance and economics compared briefly with a conventional chemical treatment system involving sludge generation and landfill disposal (Fleet et al 1986, Fleet 1988). The principle of this system is shown schematically in Figure 1. It involves integration of ion-exchange and electrolytic recovery systems to handle the range of metals and concentrations generated by the industry.

The main features of the system include:

- * Segregation of metal bearing waste streams into metal type (copper, chelated copper, tin, tin/lead, nickel etc.) and into concentration level (low concentration process rinses and high concentration process bath dumps, etchants, etc.)
- * The development of a specific recovery process for each waste stream; generally ion-exchange is used to treat the low concentration process rinses (Figure 1) and electrolytic recovery for the high concentration sources in addition to the eluates from the ion-exchange system.
- * The use of a network-integrated process control system in which the various subunits of the waste treatment system have dedicated, stand-alone microprocessor controllers which are also networked to a central supervisory controller
- * Recovery of all toxic metals (via the electrowinning system) in the form of solid metallic sheet or foil
- * The option of incorporating a demineralization system and recycling up to 95% of plant process water as high purity deionized water

Case Studies

Three printed circuit board plants of varying size and type of manufactured product were studied ranging (in terms of process water usage) from 10,000 to 100,000 gallons per day. The aims of the case studies were;

- * To examine current waste management practices
- * To evaluate the prospects for waste reduction including the use of recycling, zero-sludge technologies
- * To make specific recommendations as to how these plants could reduce their dependence on off-site waste disposal.

Each of the case studies will be reviewed briefly.

Technology Demonstration Program

Based on the results of this study, SCADA Systems was awarded a technology demonstration contract to demonstrate the technical feasibility of a zero-sludge waste management system at a Southern California printed circuit board plant (SCADA 1987). The Department of Health Services contributed \$110,000 towards a total installed system cost estimated at \$1.3M. Progress under this project will be reviewed.

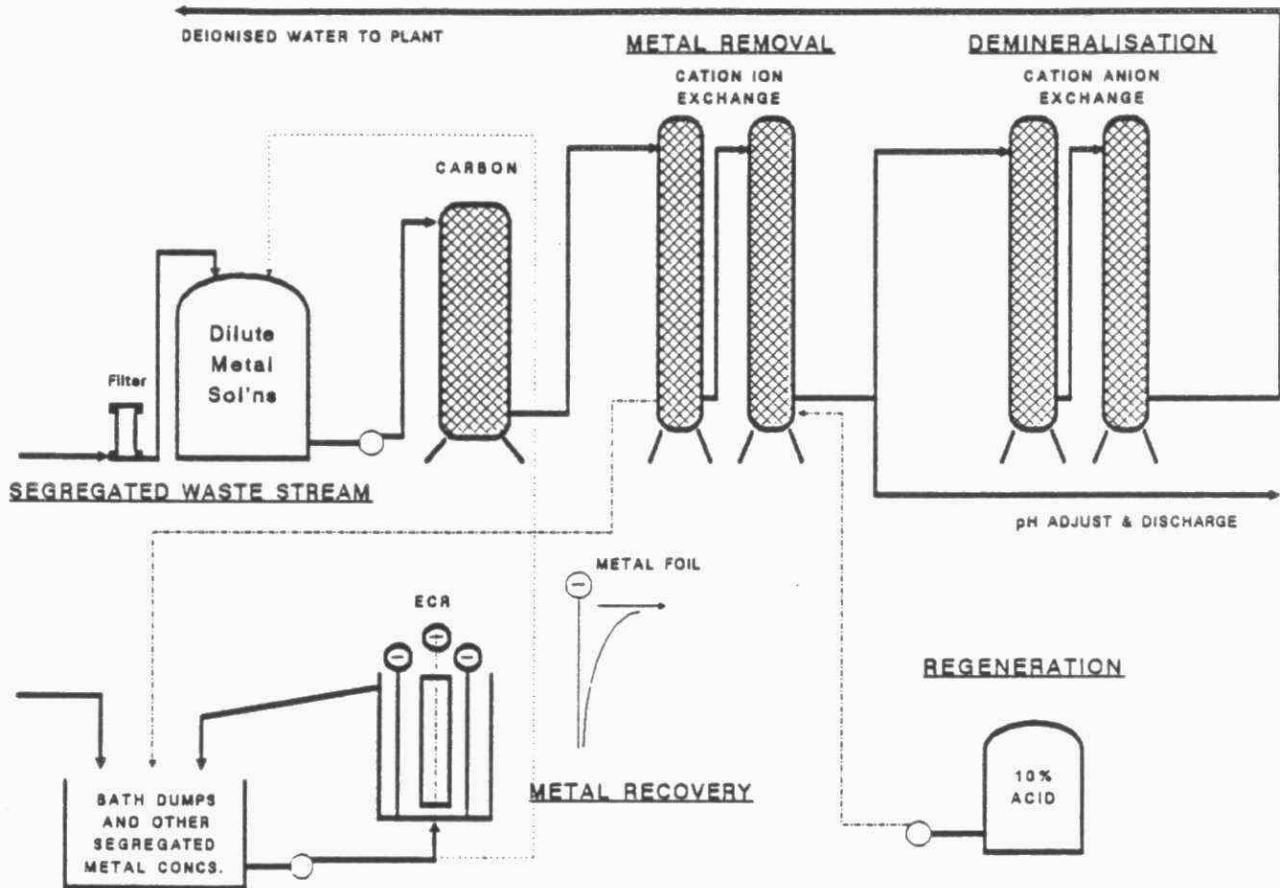


Fig 1 HEAVY METAL RECOVERY USING INTEGRATED ION-EXCHANGE/ELECTROLYTIC RECOVERY

Economics of Heavy Metal Waste Management In Canada

A current study (Fleet et al 1987a) aims to review the economic factors affecting the implementation of zero-discharge, resource recovery waste management strategies for Canada's heavy metal generating industries. This study will focus on the metal finishing, printed circuit board and gold milling industries and plans to generate an economic model to allow prediction of future waste management costs. The objectives and techniques to be used in this study will be reviewed briefly.

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EXPERIMENTS ON THE MOVEMENT OF IMMISCIBLE LIQUIDS AND THEIR VAPOURS IN SOIL.

by

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ABSTRACT

An experimental programme to study the movement of immiscible liquids and their vapours in soil has been in progress over the last three years. This paper presents current results from the study. The movement of four immiscible liquids in sandy soils has been examined with the use of laboratory scale columns. Separate measurements of capillary pressure and relative permeability were made and used with a transport model to simulate immiscible liquid movement. Two dimensional experiments to investigate fingered flow in stratified media were also performed.

Vapour movement was examined from two types of liquid sources, one a flat pool at the water table and the other a suspension in pores in the unsaturated zone. A two dimensional chamber filled with sandy soil was used for these experiments. A vapour transport model provided successful simulations of the vapour movement. The results are evaluated in the context of assessing and controlling hazardous immiscible liquids and their vapours resulting from spills and leakages into soil.

1. INTRODUCTION

This paper presents some current results of a research programme studying the behaviour of hazardous immiscible liquids in soil. The programme has been in place since 1983 in Civil Engineering at the University of Waterloo and has addressed the spreading of the liquids during a spill, their penetration and transport in the ground and the release and movement of vapours from the liquids. The work has centred on the creation of mathematical models to simulate these processes and the performance of experiments to quantify factors which affect them. This paper is the fourth in a series presented at the Ontario Ministry of the Environment's Annual Technology Transfer Seminars (Farquhar and McBean, 1984; Allan *et al.*, 1985, Farquhar *et al.*, 1986) and deals specifically with recent experimental results on liquid and vapour transport in soil. The modelling work and the experimental methodology have been presented previously.

2. BACKGROUND

The presence of hazardous immiscible liquids and their vapours in soil has been among the most troublesome problems concerning the environment in the past decade. Spills from ruptured containers, leakage from buried tanks, industrial discharges and improper disposal practices are the usual causes of these problems.

Immiscible liquids move downward through the soil leaving an interstitial residual as they go and thus creating a stationary trail from which subsequent contamination can arise. Liquids less dense than water upon reaching the zone of groundwater saturation will stay at the capillary fringe, spread laterally and move in the general direction of the groundwater. Liquids more dense than water and with sufficient pressure will enter the zone of saturation, continue to move downward to a layer which they cannot penetrate and then move laterally.

These general patterns of movement have been identified by Schwille (1975 and 1984) and others. However, there is very little quantitative information available to assess this movement or to predict how the liquids will behave under specific situations such as might be the case during remediation attempts. The same can be said for vapours which arise from the liquids.

Simulation models are extremely important in the analysis of problems dealing with immiscible liquids and their vapours in soil. In cases where the extent of migration or the effectiveness of control measurements is of concern, there is seldom sufficient time or resources to test physically, all possible conditions which might be encountered. Simulation models can provide useful information in this regard given the existence of some field information to calibrate the model. However, extensive prior testing of the model against controlled experimental data is needed to validate that the model is capable of representing real conditions.

Consequently, this research programme was undertaken in part to create simulation models which could be used in evaluating actual field conditions and also to perform experiments to assist in validating the models. The experiments were also intended to augment the general understanding of immiscible liquid and vapour transport in soil.

3. EXPERIMENTS ON IMMISCIBLE LIQUID MOVEMENT IN SOIL

3.1 Materials and Methods

Experiments were performed in which various immiscible liquids including hydraulic oil, kerosene, tributyl citrate and trichloroethylene were made to flow through previously water saturated soils specifically Ottawa sand (ASTM C-190) and a sandy silt. Most experiments were performed in a one dimensional, vertical mode using the cylindrical column shown in Figure 1. The details of the column design and operation have been presented previously (Abbott, 1987; Farquhar *et al.*, 1986) and are only briefly dealt with here.

The columns were packed with soil and fitted with two thermopropes (Abbott, 1987) to detect changes in interstitial liquid composition. The soil was saturated with the wetting fluid (usually water) and measurements of soil porosity (n) and intrinsic permeability (k) were made. The nonwetting fluid was then allowed to displace the wetting fluid and the movement of the displacement front was detected as it passed the thermopropes. The pressure differential between the two fluids was variable to allow different displacement rates and the columns could be operated in an upflow or a down flow mode depending on the relative

Figure 1 Relative Permeability Apparatus

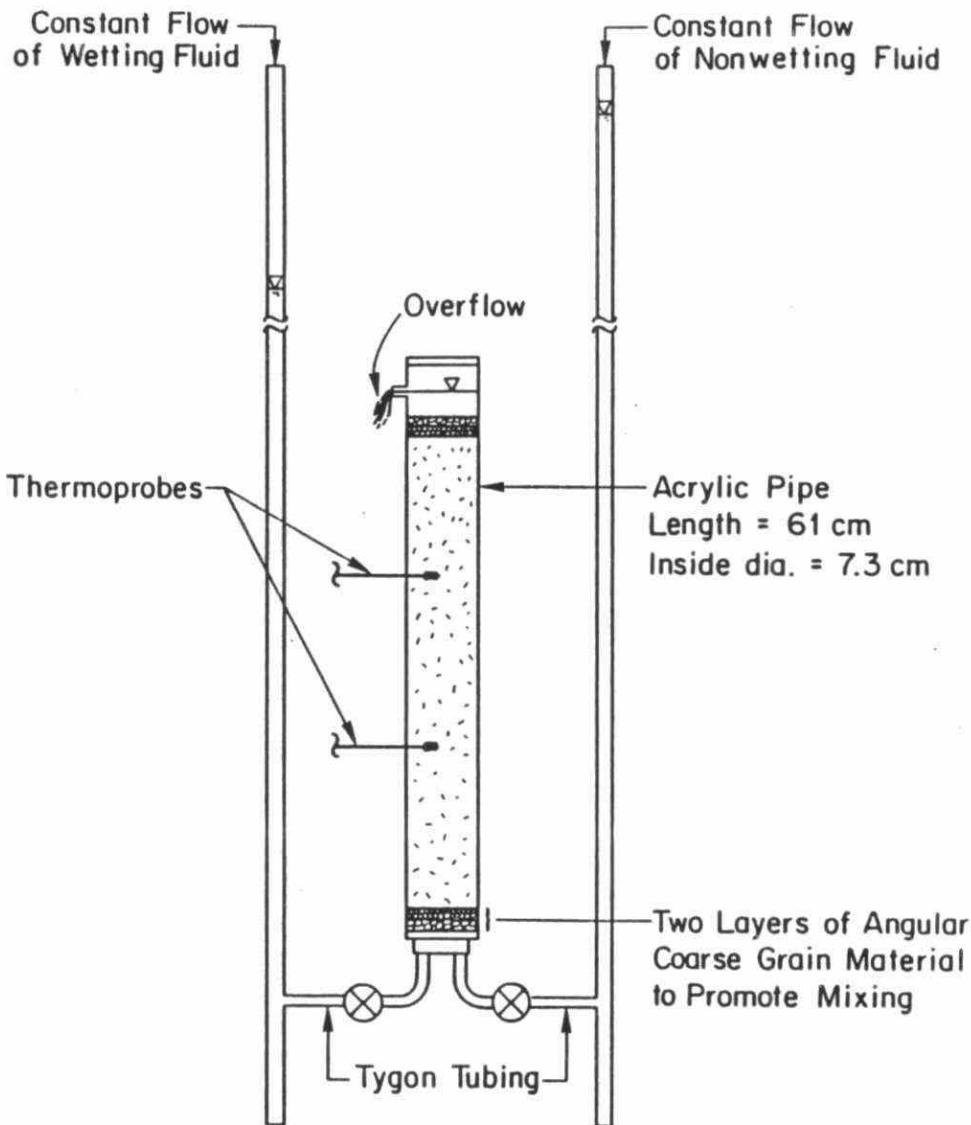
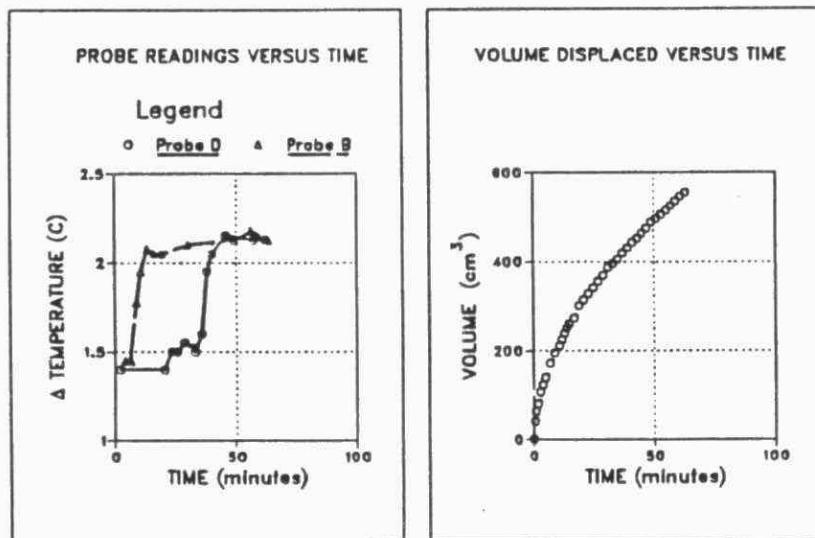


Figure 2 Experiment #5 Results

GENERAL INFORMATION		COLUMN DATA	
Date	27/10/87	Probe B	13 cm from inlet
Temperature	20° C	Probe D	31 cm from inlet
Porous Media	Ottawa Sand	Column Diameter	7.3 cm
Wetting Fluid	Water	Column Length	52.0 cm
Nonwetting Fluid	Tributyl Citrate	Inlet Pressure	$1.65 \times 10^4 \frac{\text{gm}}{\text{cm sec}^2}$
Displacement Direction	Downwards	Outlet Pressure	$5.10 \times 10^4 \frac{\text{gm}}{\text{cm sec}^2}$
FLUID PROPERTIES AT 20° C		POROUS MEDIA PROPERTIES	
Wetting fluid viscosity	1.00 Pa · sec	Intrinsic permeability	$2.06 \times 10^{-8} \text{cm}^2$
Wetting fluid density	1.00 gm/cm ³	Porosity	33.0%
Nonwetting fluid viscosity	27.0 Pa · sec	Pendular Saturation	9.1% water
Nonwetting fluid density	1.02 gm/cm ³	Insular Saturation	n/a

DISPLACEMENT EXPERIMENT RESULTS



densities (ρ) of the two liquids. In the field, upflow of immiscible liquids is rarely encountered. However from an analytical point of view, upflow was useful since it permitted the examination of a range of fluid viscosities (μ) and mass densities (ρ) while avoiding the need to work extensively with hazardous liquids. For example nonhazardous oils ($R < 1$) could be used to displace water in the upflow mode. This permitted extensive work on equipment design, methods development, and the study of basic transport properties to be conducted at low risk.

3.2 EXPERIMENTAL PROGRAMME

Displacement Experiments

A total of six displacement experiments were performed; the results from two of which are shown in Figures 2 and 3 together with experimental conditions.

Figure 2 shows the downward displacement of water in the Ottawa sand by tributyl citrate (TBC), it being more dense and more viscous than water. The graph on the lower left shows the change in liquid composition at the upper thermoprobe (B) followed by the lower thermoprobe (D). The data are given as temperature change (T =thermoprobe output) versus time. At time zero, both thermoprobes recorded $T = 1.4$ °C being exposed to 100% wetting fluid (water) saturation. As the TBC passed each probe in turn, the ΔT readings increased eventually to 2.15 °C at pendular saturation reflecting the lower thermal conductivity of the TBC as compared to water.

Although the data are somewhat scattered, they show a steep front indicating a narrow band in which the TBC displaced water from 100% to pendular or residual saturation. This was expected because of the uniform grading and thus pore size distribution of the Ottawa sand. The nonwetting fluid has greater difficulty entering smaller pores with these being filled later in the experiment and causing the curves to "tail off" with time. Since the pore sizes are more uniform than typically well graded field soils, the "tailing off" reduces creating a steep front in the curves.

The graph at the lower right of the figure shows the volume of total liquids displaced with time. The displacement rate decreases with time even though the pressure head remains constant because of the greater viscosity of the nonwetting liquid.

Figure 3 shows very similar trends for the upward displacement of water by hydraulic oil in the Ottawa sand. This was also the case for the other four experiments performed.

The results of the six experiments were of value for several reasons:

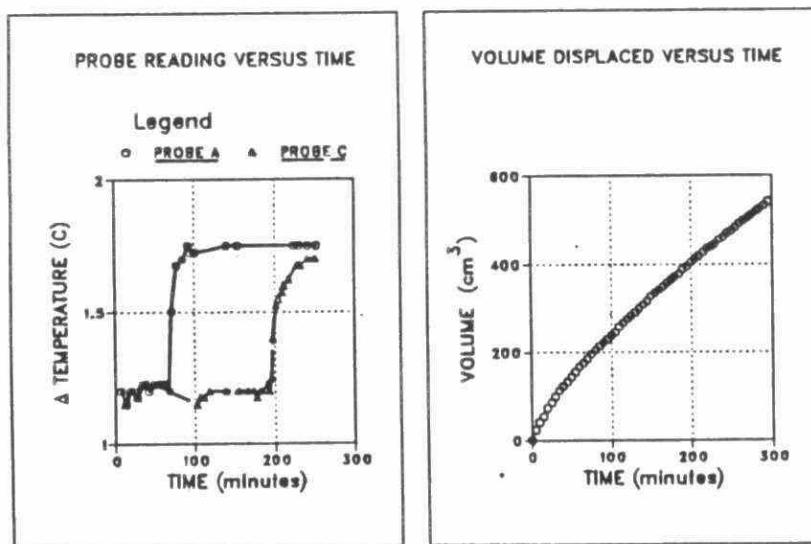
- These are among the first experiments of their kind in which in situ immiscible liquid displacement in soil was measured with respect to fluid properties, soil conditions, temperature and applied pressure gradient.

Figure 3 Experiment #2 Results

GENERAL INFORMATION		COLUMN DATA	
Date	17/09/86	Probe A	19 cm from inlet
Temperature	18° C	Probe C	37 cm from inlet
Porous Media	Ottawa Sand	Column Diameter	7.3 cm
Wetting Fluid	Water	Column Length	52.0 cm
Nonwetting Fluid	22h Oil	Inlet Pressure	$6.27 \times 10^4 \frac{fm}{cm \ sec^2}$
Displacement Direction	Upwards	Outlet Pressure	$4.41 \times 10^3 \frac{fm}{cm \ sec^2}$

FLUID PROPERTIES AT 18° C		POROUS MEDIA PROPERTIES	
Wetting fluid viscosity	1.06 Pa · sec	Intrinsic permeability	$2.00 \times 10^{-6} cm^2$
Wetting fluid density	1.00 gm/cm ³	Porosity	32.3%
Nonwetting fluid viscosity	49.5 Pa · sec	Pendular Saturation	10.0% water
Nonwetting fluid density	0.86 gm/cm ³	Insular Saturation	92.0% water

DISPLACEMENT EXPERIMENT RESULTS



- The information collected provided useful insights into the nature of immiscible liquid displacement in soil especially with regard to fingering, front development, displacement rates and pendular saturation
- The work provided development and evaluation of equipment and methods for studying immiscible liquid displacement in soil on a laboratory scale. This was particularly so for the soil column and the thermoprobe developed specifically for this work.
- The data collected were sufficiently complete to permit the testing of mathematical simulation models.

Experiments to Determine Capillary Pressure and Relative Permeability with Respect to Liquid Saturation

In order to express mathematically, variably saturated flow in porous media, it is necessary to quantify capillary pressure and relative permeability with respect to liquid saturation. There are however no capillary pressure data available for immiscible liquid pairs and only relative permeability data available for oil-water systems. There is therefore a need for such data if equations for immiscible flow are to be used. The results of this research appear to be the first data available to satisfy this need.

Capillary Pressure

Experiments were performed to generate three capillary pressure versus saturation curves for tributyl citrate and water in Ottawa sand and for hydraulic oil and water in Ottawa sand and a sandy silt soil. The equipment developed for this work was a modified form of the Haines apparatus and is shown in Figure 4. The details of the equipment and the methodology used have been presented by Abbott (1987).

The soil was packed in the cylinder and then saturated from below with the wetting fluid (air-free water) with fluid extending into the burette. The nonwetting fluid was contained in the glass and steel tubes with none in the soil at start up. As the experiment progressed, the burette was lowered incrementally, forcing some nonwetting fluid into the soil and thus displacing an equal volume of water into the burette. The fitted glass disk prevented movement of the nonwetting fluid into the burette. The displaced volume measured in the burette was used to calculate the percent saturation of the two liquids in the soil while the difference in the elevation of the two fluids was equal to the capillary pressure (P_c) at that saturation. This was then repeated for further reductions in burette height.

The capillary pressure plots produced are shown in Figure 5 for the main drainage curve and a portion of the imbibition curve. The central portion of the curves involving Ottawa sand have a near zero slope as expected because of the pore size uniformity. The curves for the other soil have a much greater slope in the central region because of the greater pore size distribution.

Figure 4 Capillary Pressure Apparatus For Liquids Heavier Than Water

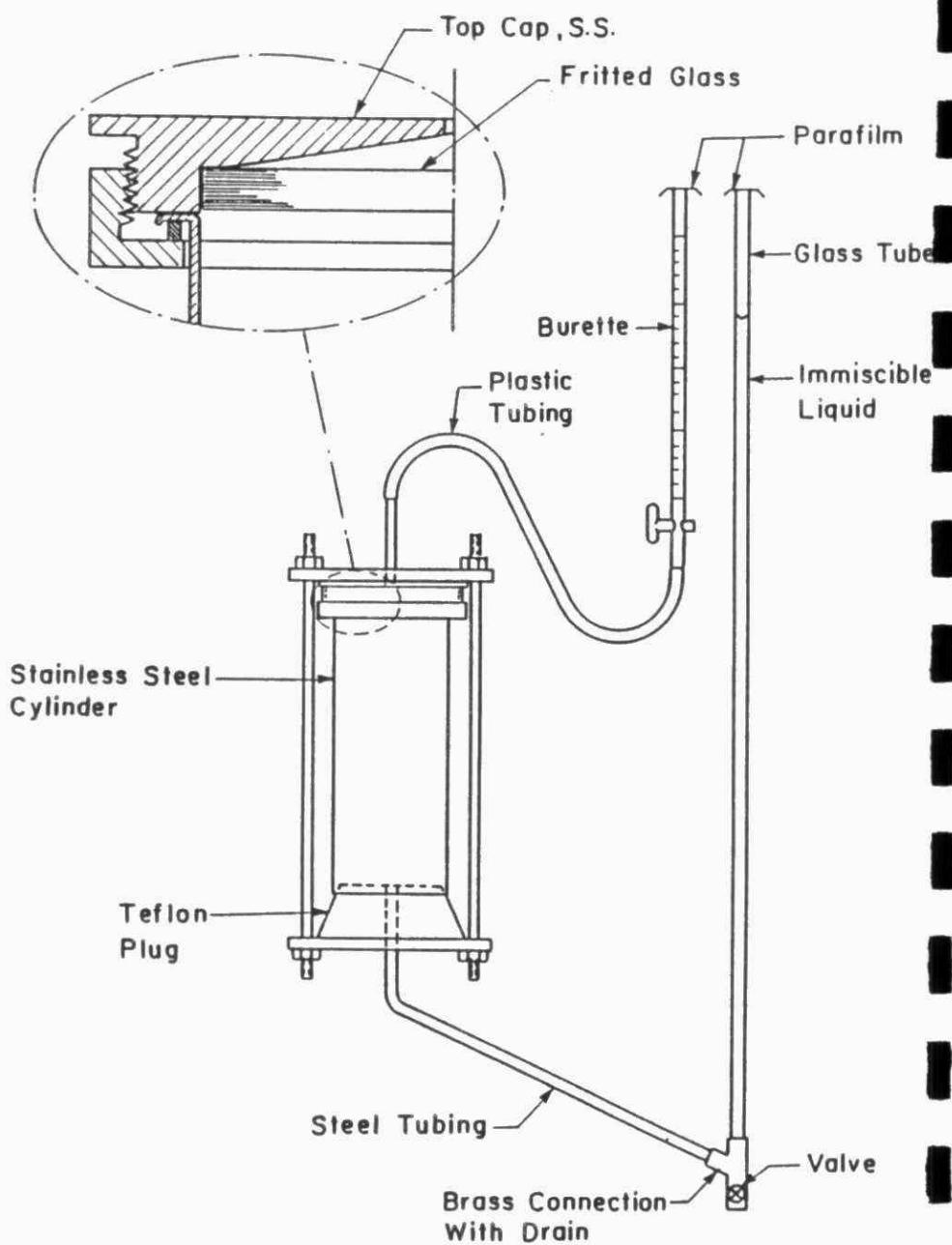
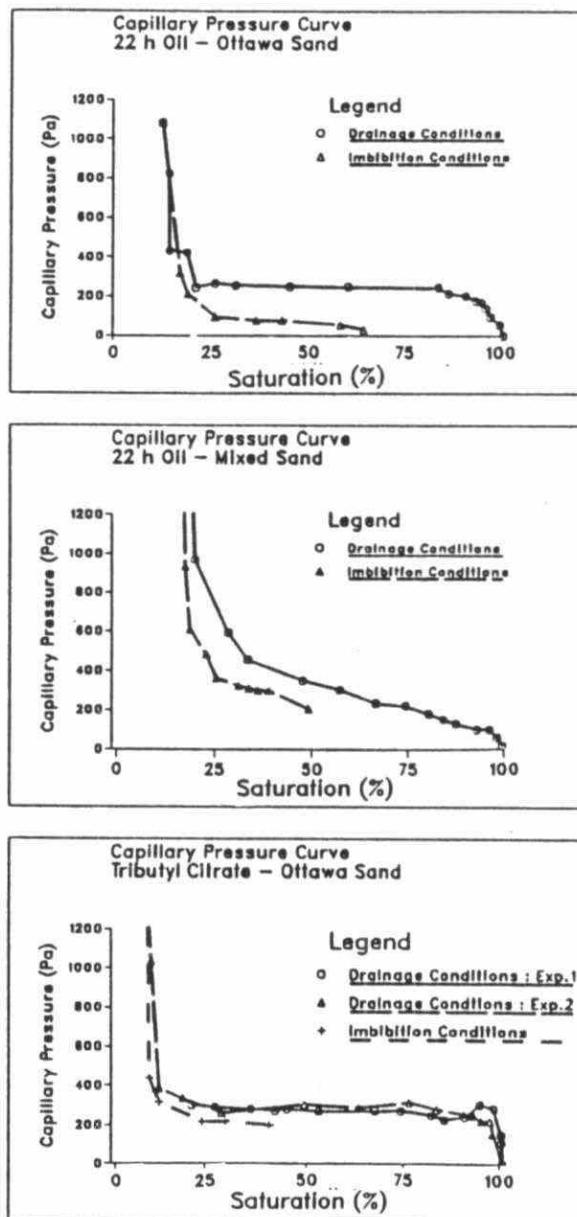


Figure 5 Capillary Pressure Curves



The main drainage curve for tributyl citrate displacing water in Ottawa sand was repeated (Exp. 2 replicates Exp. 1) and the data from both experiments are presented in the bottom graph. Although there is some scatter in the data, the curves appear to be reproducible.

The capillary pressure curves were used subsequently to model the displacement experiment results.

Relative Permeability

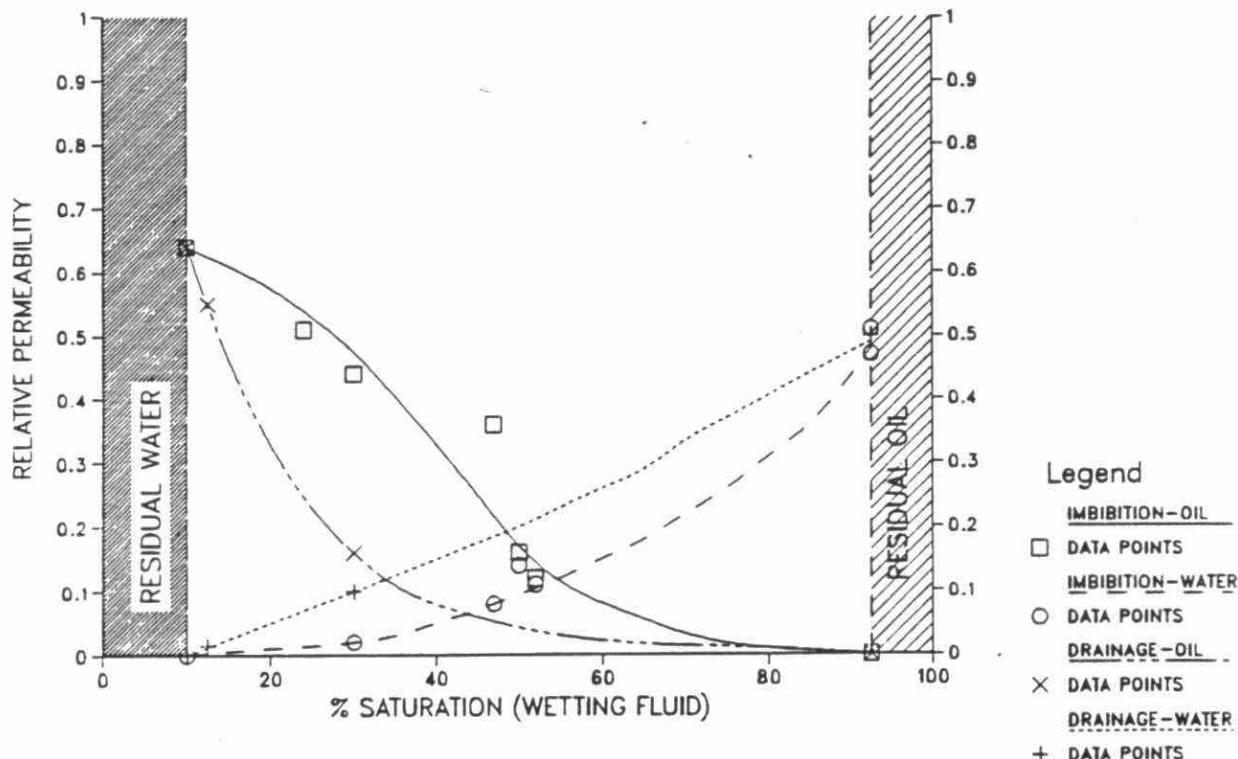
One relative permeability experiment was performed involving oil and water in Ottawa sand. The equipment was the same column used in the displacement experiments (Figure 1). The detailed methodology is presented in the work of Abbott (1987). In general, the procedure consisted of equilibrium, continuous flow experiments in which the wetting and nonwetting fluids were made to flow through the soil concurrently. Different flow rates were produced by varying the relative pressures applied to the two liquids. Thermoprobe were used to measure the relative saturations of the two liquids within the soil. Outlet discharge rates were measured to obtain the flow rates of the individual liquids. The relative permeability curves produced are shown in Figure 6. They are of a form similar for those obtained for air-water systems but are among the few available for liquid-liquid pairs in soil. The number of data points is limited because the time required to obtain a single point ranged up to 24 hours.

Three problems were identified using the relative permeability measurement experiments: the length of time required to create a set of curves is substantial (two and one half weeks in this case); the large volumes of liquid required detracts from the utility of the method for hazardous liquids; the high flow velocities needed to minimize end effects in the column introduced an error ($\pm 10\%$) in the thermoprobe readings (see data scatter in Figure 6). Consequently, alternative means to obtain relative permeability information were evaluated. The Burdine equation (Burdine, 1953) which uses the drainage capillary pressure curve and relative permeability at pendular saturation to estimate the drainage relative permeability curve, was found to produce acceptable results. It was used for the other liquid pairs of this study.

3.3 MODEL SIMULATION OF IMMISCIBLE LIQUID DISPLACEMENT EXPERIMENTS

Two immiscible liquid displacement models were examined to evaluate their suitability for simulating the experimental results of this research. One was the two dimensional, finite element numerical model (WSTIF) produced by Osborne and Sykes (1986). This model makes use of capillary pressure and relative permeability curves as produced in this work. The other suggested by McWhorter (1986), was a one dimensional analytical model using the capillary pressure curve as a step function. The complete model analysis performed is given in the work of Abbott (1987).

Figure 6 Relative Permeability Curve



The model simulations ranged from good to fair and appeared to be influenced significantly by the quality of the capillary pressure curve in the region of the bubbling pressure. In general the numerical model performed better than the analytical one. An example of the simulations is shown in Figure 7. The experiment consisted of the upward displacement of water by oil in the sandy silt soil. The agreement between the numerical model (WSTLF) simulation and the experimental data is reasonably good considering that the model was not fitted to the data. Rather, the model was run independently using input data such as capillary pressure, relative permeability and boundary condition data as collected in the experiments. The results of the simulation study were encouraging because they showed that the numerical model of Osborne and Sykes provides reasonable simulations of real systems. The model appears to have potential for use in field situations where estimates of immiscible liquid transport are required.

4. EXPERIMENTS ON THE MOVEMENT OF HAZARDOUS VAPOURS IN SOIL

Experiments were conducted to study and to quantify the movement of vapours produced from hazardous immiscible liquids in soil. In addition to providing a better understanding of vapour movement, the data were also to be used to test the numerical vapour transport model developed by Allan (Allan, 1986). The results from this study are described in detail in work by Kell (1987).

4.1 MATERIALS AND METHODS

Vapour transport experiments were performed in a one dimensional column and a two dimensional flux box as shown in Figures 8 and 9 respectively. The design and operation of these units are described elsewhere (Farquhar, et al., 1987; Kell, 1987). The columns were 7cm in diameter and 36cm high and allowed a vapour source (either gas or liquid) to be located above or below the soil. Vapour sample collection and pressure measurements were possible at ports along the length of the column. The flux box was 3.6m long, 1.2m high and 0.3m wide and could accommodate a vapour source at the base in the centre or within the soil itself. Sample and pressure measurement ports were located throughout the soil. Vapours were vented only at the soil surface.

The soil used in both sets of experiments was an Ottawa sand for which the following properties were measured at 20°C:

Intrinsic Permeability (k)	$1.45 \times 10^{-11} \text{ m}^2$
Porosity (n)	0.35
Organic Content	0.17% dry wt
Water Content	0.035% dry wt
Density-Uncompacted	89.1 lb.ft^{-3}
-Compacted	93.5 lb.ft^{-3}

Figure 7 Modelling Results for Experiment #6

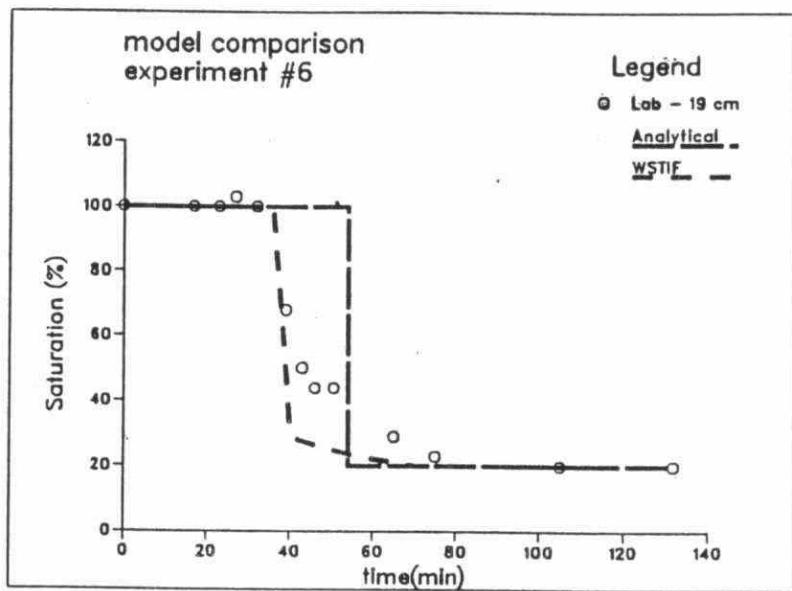
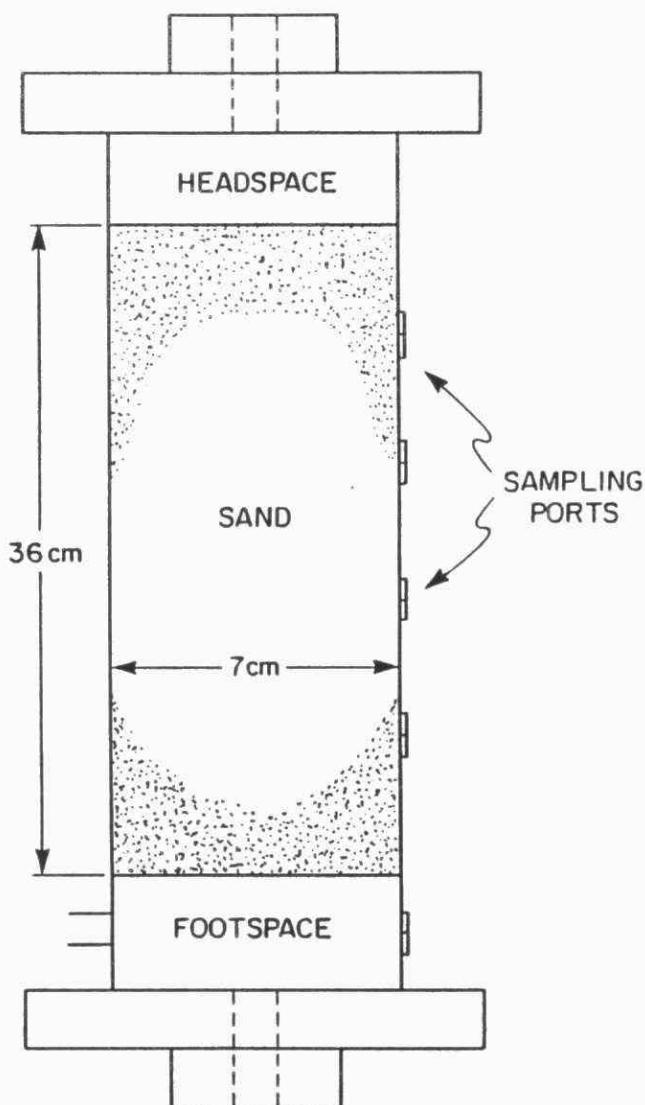
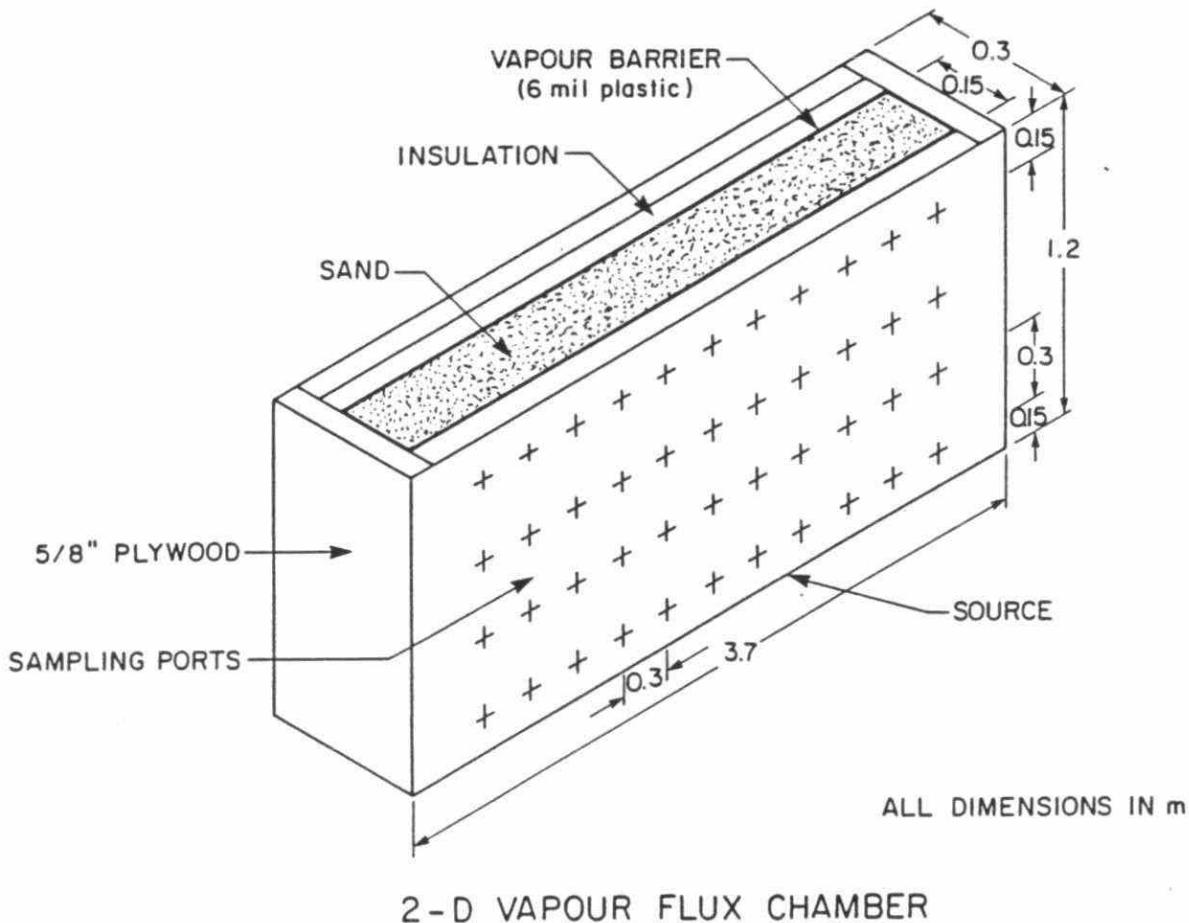


Figure 8



1-D VAPOUR FLUX COLUMN

Figure 9



Eighty eight percent of the sand was retained on U. S. Sieve numbers 70 (30%), 100 (38%) and 140 (20%).

The vapours studied are summarized below:

Property (20°C)	Pentane	Acetone	Methane
Vapour Pressure (atm)	0.575	0.237	-
Molecular Diffusion in Air ($m^2 \cdot s^{-1}$)	7.1×10^{-6}	1.26×10^{-5}	1.66×10^{-5}
Viscosity (Pa.s)	6.7×10^{-6}	7.3×10^{-6}	1.05×10^{-5}

4.2. COLUMN EXPERIMENTS

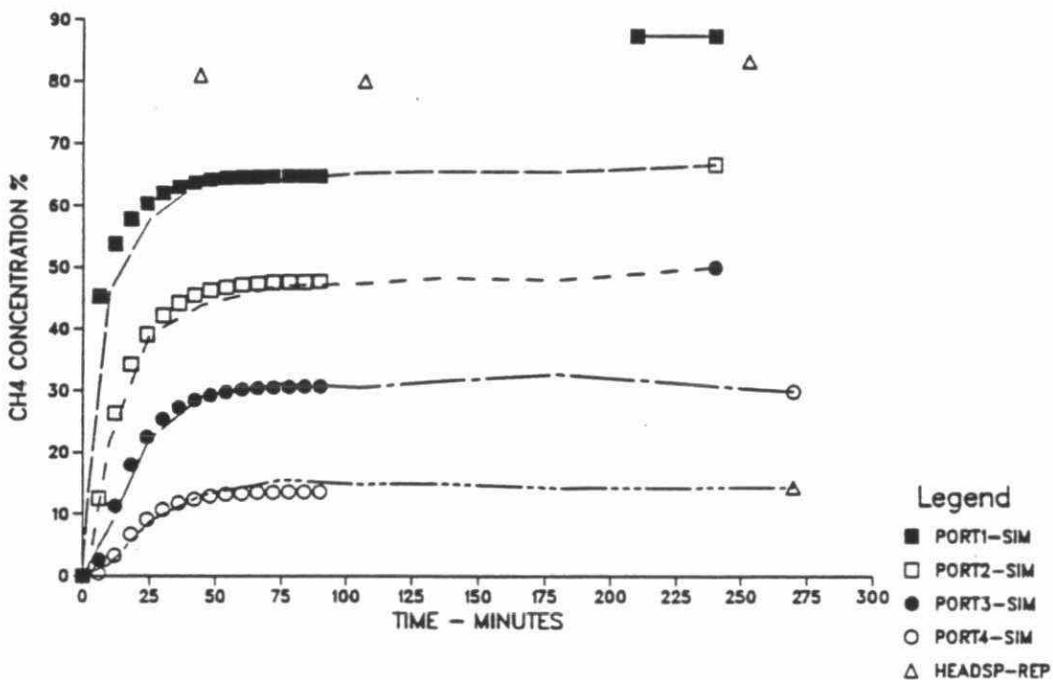
A series of column experiments was performed in the early stages of the research to assist in developing methods and exploring trends in vapour transport in soil. These followed the same general pattern with a liquid source at either the top (headspace) or the bottom (footspace) and pressure and vapour concentrations being measured during transport. Two sets of results are provided as examples of the results obtained. In each case, the vapour source was in the head space and the objective was to observe the downward movement of the vapours into sandy soil. No pressure gradient was applied across the soil samples; thus diffusion and body forces (relative density effects) would be responsible for vapour migration downward. In all cases, the footspace was maintained with zero vapour concentration through the use of an air purge.

The vapour sources included methane gas at 82% by volume and liquid pentane with 32% vapour in the head space. Pentane vapour is more dense than methane and air while methane is less dense than air. The impact of these density variations on vapour transport is shown in Figures 10 and 11 for methane and pentane respectively. The lines in the Figures represent actual data; the symbols are simulations performed with the Allan model. The information is presented as percent vapour at each of four sampling ports (port 1 is near the top of the soil sample, port 4 is near the bottom).

In the case of methane (Figure 10), there is a linear gradient of vapour concentrations from the top to the bottom of the sand. This indicated that diffusion alone was producing movement. This is consistent with the fact that methane is less dense than air and therefore body forces would not contribute to downward movement. The methane concentrations became steady after approximately 50 minutes.

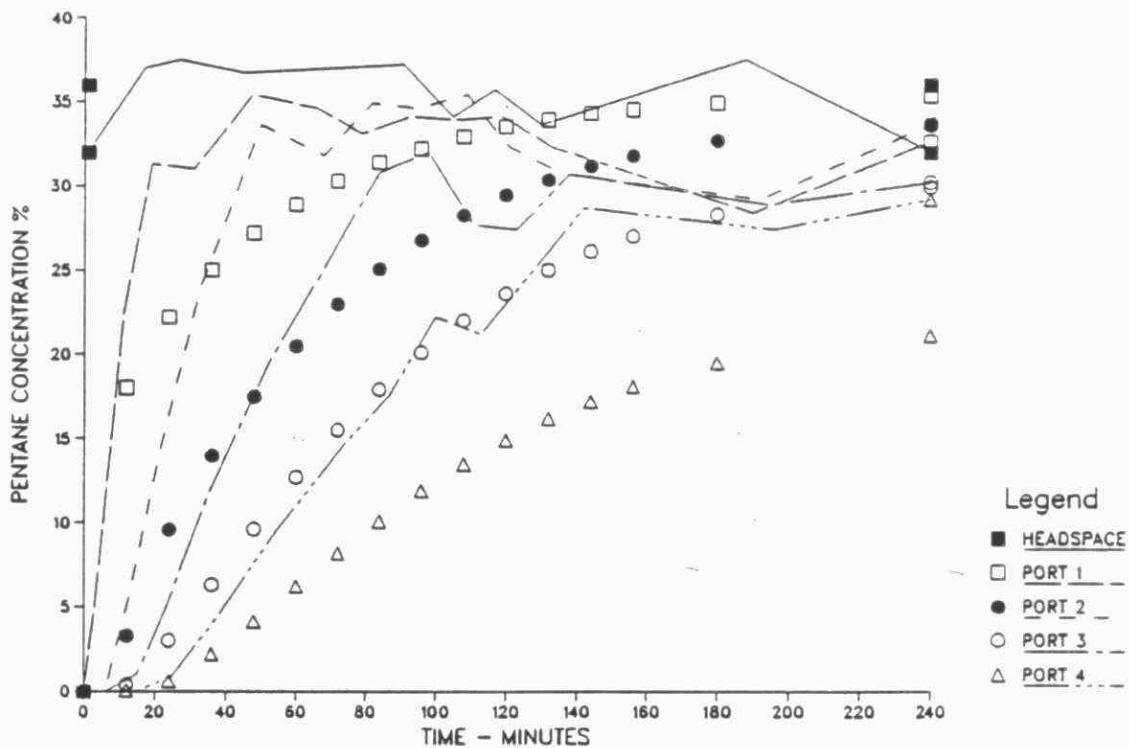
In contrast, the pentane data (Figure 11) showed two opposite trends. First, all ports eventually exhibited concentrations approximately equal to the source as opposed the uniform gradient produced with methane. Since pentane is more dense than air, both diffusion and body forces worked to drive the pentane vapours to the base of the soil. Second, since the diffusion coefficient of pentane is approximately one half that of methane, the time to reach steady concentrations was about 140 minutes, much longer than the 50 minutes for methane.

Figure 10: CH₄ MIGRATION - EXPERIMENT 3 SIMULATION



82% HEADSPACE

Figure 11: PENTANE MIGRATION SIMULATION



EXPERIMENT #5, JULY 15, 1987
 $K=5 \times 10^{-11}$

The model simulations for the methane are excellent. They are not as good for pentane and this appears to have been due to the use of an assumed permeability for the pentane since measurements were not made at the time of experimentation.

4.3. FLUX BOX EXPERIMENTS

Eight flux box experiments were performed during the investigation, seven with the vapour source below the sand at the centre of the box and one with a vapour source located 45 cm below the surface of the sand. The following conditions were the same for all experiments.

- Maximum temperature variation within the soil was .5°C in response to changes of up to 5°C in room temperature outside the box.
- All experiments involved diffusion only. No pressure gradients between the source and the discharge surface could be detected.
- Daily atmosphere pressure variations were less than 5mm Hg.

The results of two experiments are presented here as examples of the work done.

Liquid Pentane as a Vapour Source at the Base

Liquid pentane at an average temperature of 23.5°C was placed as an open source at the base of the box. Vapours were allowed to enter the previously air filled soil for 75 hours. The vapour concentrations (% by volume) measured at 24 and 72 hours in the soil are presented as contours in Figure 12 for half of the box (symmetry assumed). The outward movement of the pentane vapours is shown in the comparison of the two graphs. Since pentane vapours are more dense than air, the upward motion was due entirely to diffusion with discharge occurring at the open soil surface. Measurements taken after 72 hours indicated that the contours had reached a nearly steady position. The concentration of pentane vapour in the soil immediately above the liquid source was approximately 18% by volume.

The Allan Model (Allan, 1986) was tested to determine whether or not it could successfully simulate the pentane data. The model consists of two dimensional, finite element solutions of the flow (Darcy Equation) and continuity equations. The boundary conditions and the input parameters for the soil, air and pentane were those determined for the experiments themselves. Appropriate grid spacings and time steps were estimated but the model was not fitted to the data. The results of the simulations at 25 and 75 hours are shown in Figure 13. The comparison between these simulations and the actual data (Figure 12) are extremely good and provide verification that the model is capable of producing accurate simulations of vapour transport in two-dimensional soil configurations.

Other Vapours

Similar experiments and simulations were performed using methane and liquid acetone as sources. The results from the methane work were of the same good quality as those presented for pentane. The acetone simulations did not match the experimental data however. They produced a more rapid migration than observed in the experimental data. It is known that polar

Figure 12 Pentane Experiment
With Bottom Source

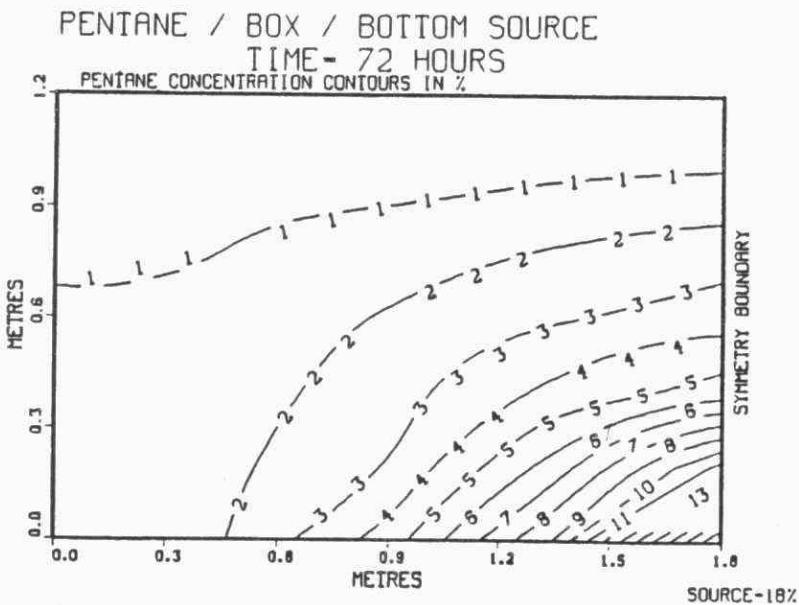
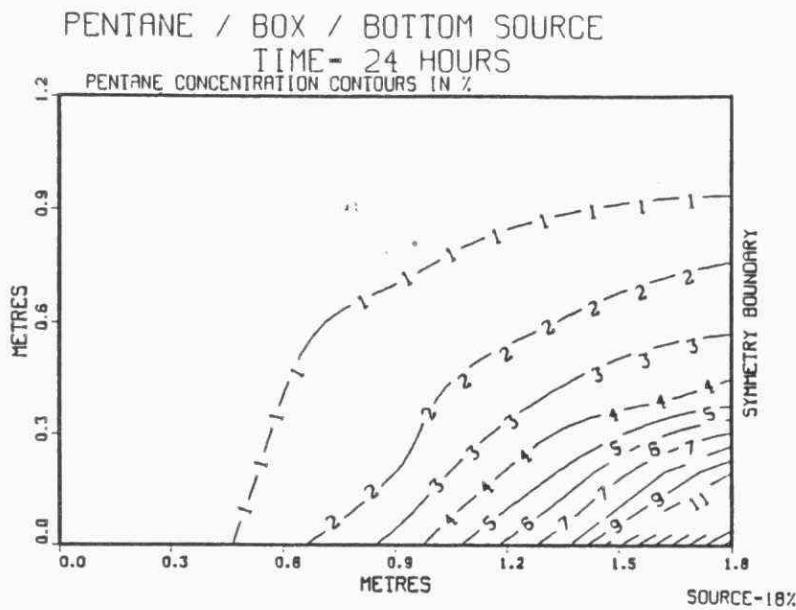
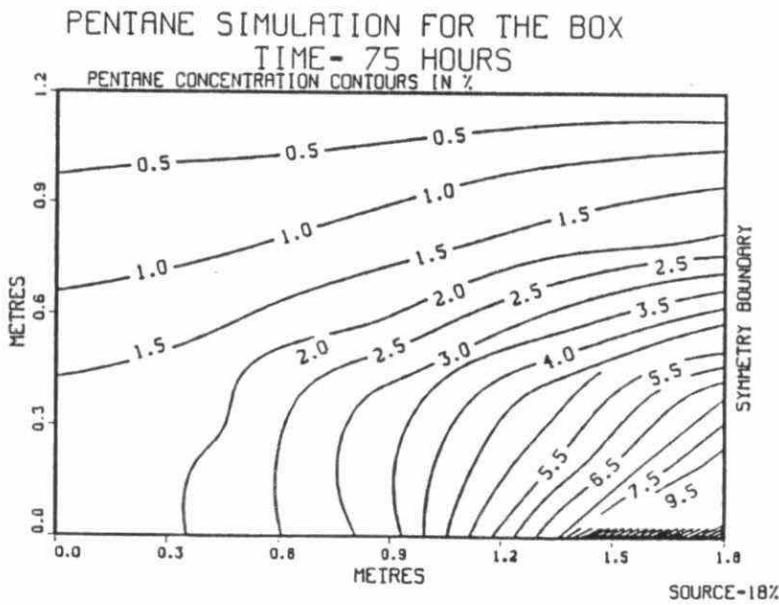
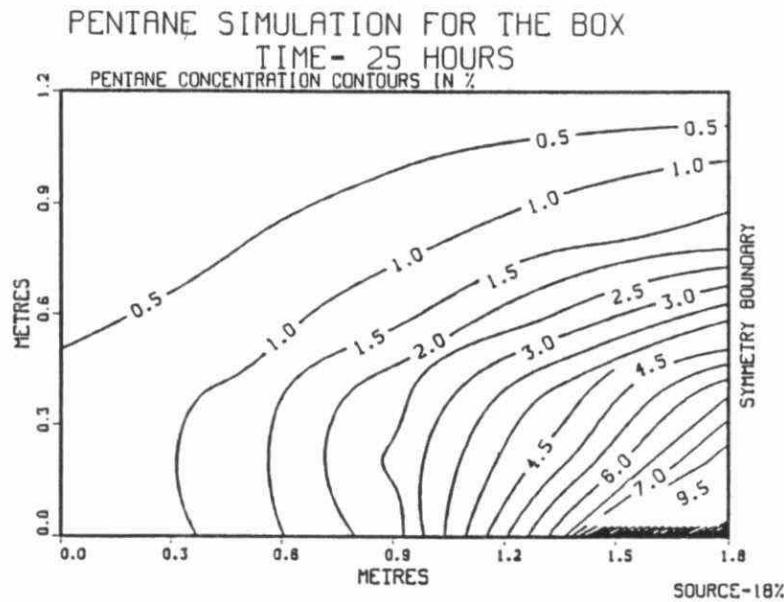


Figure 13 Pentane Simulation
For Bottom Source



vapours such as acetone tend to adsorb onto dry soils much more readily than nonpolar vapours like pentane.

Consequently, since this soil was very dry. (0.035% H₂O dry wt), extensive adsorption of acetone is likely to have occurred. Although the Allian model has a component to allow for the introduction of adsorption, no isotherm data have been found to include in the simulations. As a result, no adsorption was included. Experiments are currently in progress to quantify acetone adsorption on to the experimental soil.

Pentane as a Vapour Source Suspended in the Soil

Experiments were performed where pentane vapour was introduced in the middle of the box. A teflon pipe with holes was inserted into the soil, 45cm down from the open surface. A pentane vapour source was connected to this pipe. This then served as a suspended source for vapour migration. Measurements were then taken to detect pentane vapours throughout the soil regime. The data collected are presented in Figure 14. They show that the denser pentane vapours drifted downward due to both diffusion and body forces and then moved laterally at the sealed base of the box. Evidence of diffusion upward to the open soil surface is also provided by the vapour concentration contours.

The tendency observed here is that denser vapours can penetrate deeply into unsaturated soils and then move laterally at the water table or some poorly permeable stratum. This has major implication in field situations.

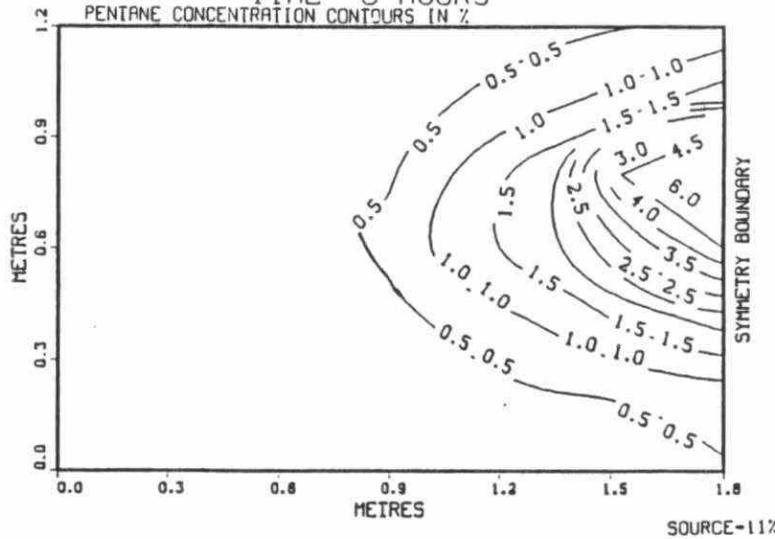
5. DISCUSSION

The objective of the research programme of which the work described here forms a part, has been to study the behaviour of hazardous immiscible liquids and their vapours in soil. This study has involved: an extensive review of relevant literature; the development of simulation models based on process fundamentals for spill formation, liquid penetration of soil and vapour transport in soil; the design and performance of experiments to quantify spill formation and liquid and vapour transport in soil. Although many problems remain to be solved in specific areas, the work has been generally successful in meeting these objectives.

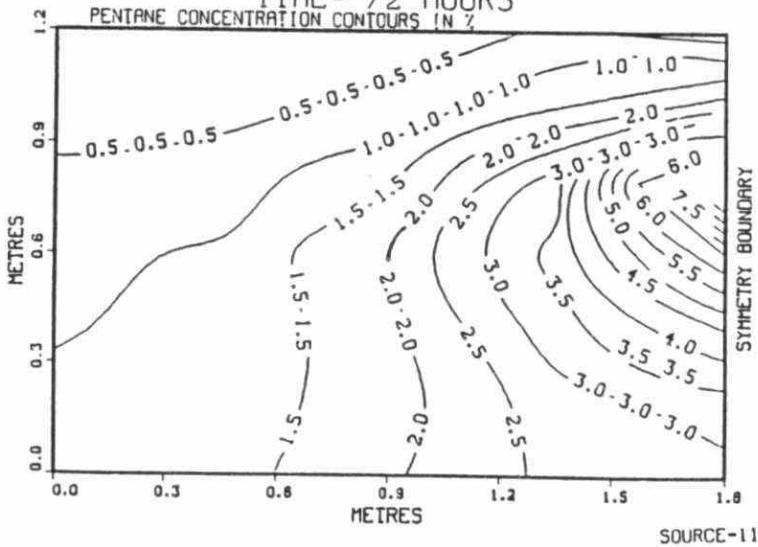
In this paper, the results of experiments on liquid and vapour transport in soil have been presented in part. In many cases, the data are the first of their kind to have been presented. They explain or corroborate many of the factors which influence this transport. They have served to validate the theoretical models produced to assist in evaluating field conditions. In addition, they have been produced with equipment and methods which can now be used for further work with other immiscible liquids in other soils.

Figure 14 Pentane Experiment
With Middle Source

PENTANE / BOX / MIDDLE SOURCE
TIME - 6 HOURS



PENTANE / BOX / MIDDLE SOURCE
TIME - 72 HOURS



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Hazardous Organic Chemicals in Groundwater
at Ontario Landfills

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ABSTRACT

The occurrence and mobility of organic contaminants in groundwater has been evaluated at seven sites in Ontario. An overview of the results will be presented. Two sites on Canada Forces Base Borden will be discussed more extensively.

The "Borden" site is situated upon an unconfined sand aquifer. It was operated from about 1940 to 1973, receiving mainly construction debris and some domestic and commercial wastes which were periodically burned. The "New Borden" landfill site has been operated since 1976. It is situated upon less permeable silty sand till. The waste is landfilled in cells without burning. Although an extensive inorganic plume emanates from the Borden landfill, very little organic material is found in this plume. This probably reflects the nature of the landfilled material and the periodic burning of the refuse.

A much less extensive plume emanates from the New Borden landfill site, reflecting the lower groundwater velocity. Numerous organics of concern have been recognized in this plume, including chlorinated

hydrocarbons, and aromatic hydrocarbons. Sorptive retardation does not seem to provide a major control on the organic mobility. Biotransformations seem to be the major attenuating process. Interpretations are complicated, however, by the temporal variability of both leachate character and organic contaminant distributions in the plume. These aspects are still being examined.

INTRODUCTION AND OVERVIEW

For the past four years researchers at the Institute for Groundwater Research have been examining the occurrence of organic contaminants in groundwaters at six sanitary landfill sites and at one waste disposal facility in southern Ontario. The purposes were to determine what organics are contaminating groundwaters, how rapidly these contaminants travel in groundwater and how persistent these organics are. The landfill sites selected represent a variety of hydrogeological conditions and so were expected to be representative of most sanitary landfill sites in southern Ontario. Also, most sites had been previously studied, so that their hydrogeology and some aspects of existing contamination were already known.

The locations of the landfill sites investigated in this study are shown in Figure 1. Three of the sites were located upon permeable, unconsolidated sand deposits in which groundwaters could move laterally quite rapidly (10 cm to 1 m per day). Thus, at the Borden, Woolwich and North Bay sites plumes of groundwater contamination extend for 800 to 1000 m from the sites. The New Borden site is located upon less permeable unconsolidated sandy till material in which groundwater moves laterally at about 35 m per year. Thus the contaminated groundwaters extend less than 250 m from this 10 year old site. The facility

operated by Tricil Limited is situated upon thick clayey deposits and the contamination extends only about 1 m from the waste.

The remaining two sites - Bayview Park and Upper Ottawa Street - are situated upon sedimentary bedrock. Unlike the unconsolidated materials, these are extensively fractured and the fractures, where open, provide the major conduits for groundwater flow. Rather than moving through the mass of interconnected pores as in sands, groundwater flows mostly along interconnected fractures, often bypassing cubic metre volumes of rock.

The dominant organics found in leachate plumes emanating from six landfills are summarized in Table 1. The organic acids were dominant, resulting from the anaerobic breakdown of organic refuse. The most significant contaminants were volatile, chlorinated, one- and two-carbon hydrocarbons (halocarbons) and volatile aromatic hydrocarbons including benzene, toluene, xylenes, chlorobenzenes and other substituted benzenes. Other commonly detected compounds included non-chlorinated solvents such as acetone, tetrahydrofuran and 1,4-dioxane. Significant occurrences of most other organics on the EPA's priority pollutant list were rare. Either these were not significant components leaching from the refuse or they did not persist into the leachate-impacted groundwaters. However, it must be remembered that exhaustive leachate characterization was not the objective of this study and so some organics of specific concern might not have been identified. Many organic components (GC/MS peaks) were not identified at each site.

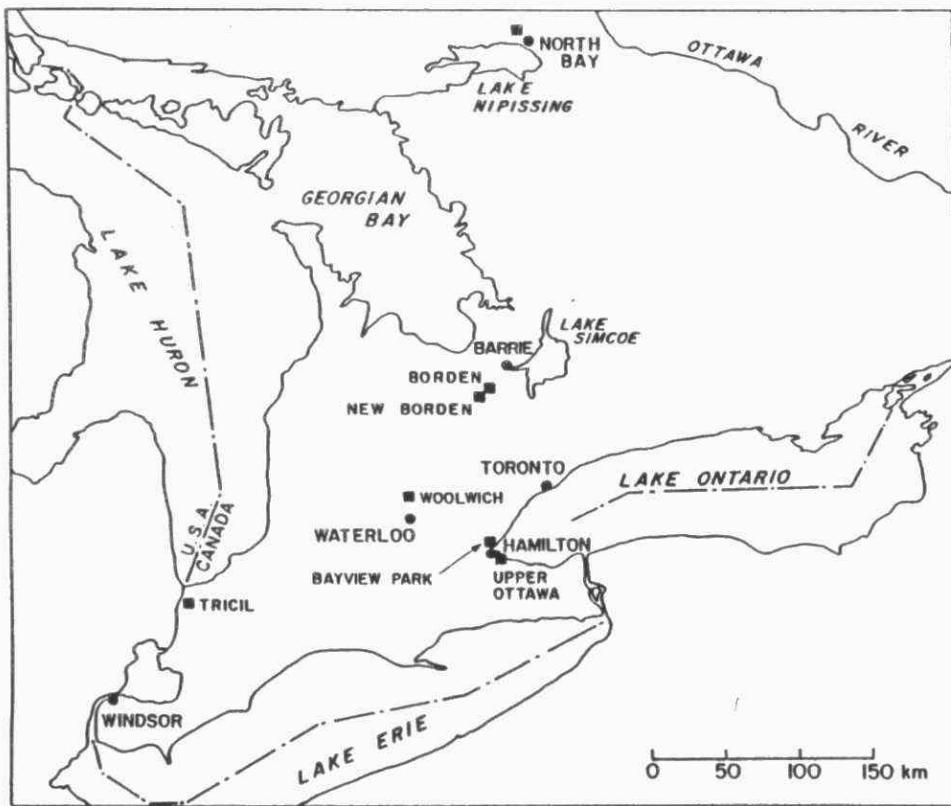


Figure 1. The location of the seven landfill sites.

Table 1: The approximate maximum concentration ($\mu\text{g L}^{-1}$) of selected organic contaminants found in leachate-contaminated groundwaters at six landfill sites. Many concentrations are only approximate.

Contaminant	Landfill Sites					
	Borden	Woolwich	North Bay	New Borden	Upper Ottawa Street	Tricil
Aliphatic, aromatic and carboxylic acids	20	>10,000	>300	-	>1000	-
carbon tetrachloride	<1	5	<1	9	p	n.d.
chloroform	<1	20	<1	25	5	n.d.
trichloroethylene	1	37	2	750	p	n.d.
trichloroethane	n.d.	7	<1	90	20	8.44
tetrachloroethylene	n.d.	2	<1	<1	<1	n.d.
acetone	<1	-	6	-	6	-
tetrahydrofuran	p	-	9	-	200	-
1,4-dioxane	n.d.	-	<1	-	p	-
benzene	3	70	51	50	60	7920
toluene	1	7500	60	1400	2600	9520
xylanes	<1	700	140	500	3500	-
ethylbenzene	<1	1100	64	120	700	3320
2,4-,2,4-trimethylbenzene	n.d.	10	250	70	450	-
chlorobenzene	n.d.	n.d.	105	n.d.	110	-
dichlorobenzenes	<1	n.d.	13	n.d.	5	-
naphthalene	n.d.	50	15	260	p	2350
phenols	-	1100	10	p	p	-
benzothiazoles	<1	30	10	n.d.	p	-
PAH's	-	-	n.d.	-	n.d.	-
phthalates	<1	p	110	p	p	-

p : detected but concentration not estimated

n.d. : not detected

- : not determined

All leachate-derived solutes were found to undergo significant dilution or attenuation as they migrated from the landfills. Much of the observed decreases in concentration must be attributed to the process of dispersion - the mixing of leachate and background groundwater that occurs throughout the solute transport domain. For organic contaminants, two other processes can also bring about lower concentration. Sorption, essentially by solid organic matter in aquifer material can both lower the solution concentration and retard the migration of sorbing solutes. The second additional attenuating process is biotransformation or biodegradation. Microbes convert the organic compound to simple inorganic molecules such as CO₂, H₂O or CH₄ usually, but this conversion may be to other organic molecules under some conditions. Chemical transformations such as hydrolysis or reductive dechlorination are also possible, but for the organics emphasized in this study, the major transformation is thought to be microbial.

In the very permeable sand aquifers at North Bay and Woolwich, dispersion seems to have brought about a very significant dilution (10 to 100-fold decreases) of all leachate parameters over the 800 m to 1000 m travel distances found at these sites. The halocarbons and volatile aromatics seem to have undergone even greater attenuation than chloride, attributed mainly to biotransformation reactions.

Biotransformations appear to be a dominant control over the behaviour of halocarbon and volatile aromatic contaminants in these landfill leachate plumes (Tricil situation excepted). Where significant organic loading to the leachate occurs (all but Borden landfill) the initial environment is likely extremely anaerobic. This promotes methanogenic bacteria which have excellent potential to biotransform halocarbons (Wilson and McNabb, 1983) but only a minor potential to biotransform volatile aromatics (Wilson et al., 1986). In some leachate plumes (Woolwich, perhaps New Borden), aerobic conditions may exist in the distal portions where leachate mixes with large ratios of oxygenated, natural groundwaters. In such an environment, aerobic bacteria can be expected to rapidly biotransform aromatics. It is not surprising, therefore, that some evidence for biotransformation of halocarbons and volatile aromatic contaminants is found within six of the seven leachate plumes investigated. This may be the major safeguard in the groundwater environment that will continue to limit the environmental impact of mobile organic contaminants in these sanitary landfill leachates.

A more detailed presentation of the results of this study can be found in Barker et al. (1987). Reinhard et al. (1984), Barker et al. (1986), and Barker (1987), discuss more specific aspects of this research. As well, a number of publications are in preparation or in review.

THE BORDEN LANDFILL

Landfilling at the Borden site was conducted from 1940 to 1976 with little onsite management prior to 1973. It received mainly wood and construction debris (80%) with the remainder being domestic and

commercial food refuse (Gartner Lee Associates, Ltd., 1977). Prior to 1973, refuse was periodically burned and covered with sand. In 1973, modern landfilling practices were employed and continued until the site was closed in 1976 when a final cover of about 0.5 m of sand was added.

Hydrogeological studies were begun in 1974 by Gartner Lee Associates and a long-term program of detailed research was initiated in 1976 when researchers from the University of Waterloo joined the study team. Much of the research results was presented in a special issue of the Journal of Hydrology (vol. 63, no. 1 and 2, 1983). The plume development, movement and inorganic geochemistry were emphasized.

In 1981 additional sampling of selected piezometers was conducted as part of a joint University of Waterloo - Stanford University study of organic contaminants in groundwaters. This paper describes the distribution of organic contaminants in groundwaters in the Borden landfill leachate plume as found in 1981.

Site Hydrogeology, Groundwater Sampling and Organic Analyses

The Borden landfill was located upon an unconfined sand aquifer. Groundwater has apparently mounded into the refuse and a plume of leachate contamination has been recognized to extend almost 700 m north of the landfill site by 1979 (Figure 2). In the cross-section along the general flow direction A-A' (Figure 3), the leachate is seen to impact only the upper, unconfined sand aquifer. A less permeable clayey till unit apparently restricts the downward movement of leachate.

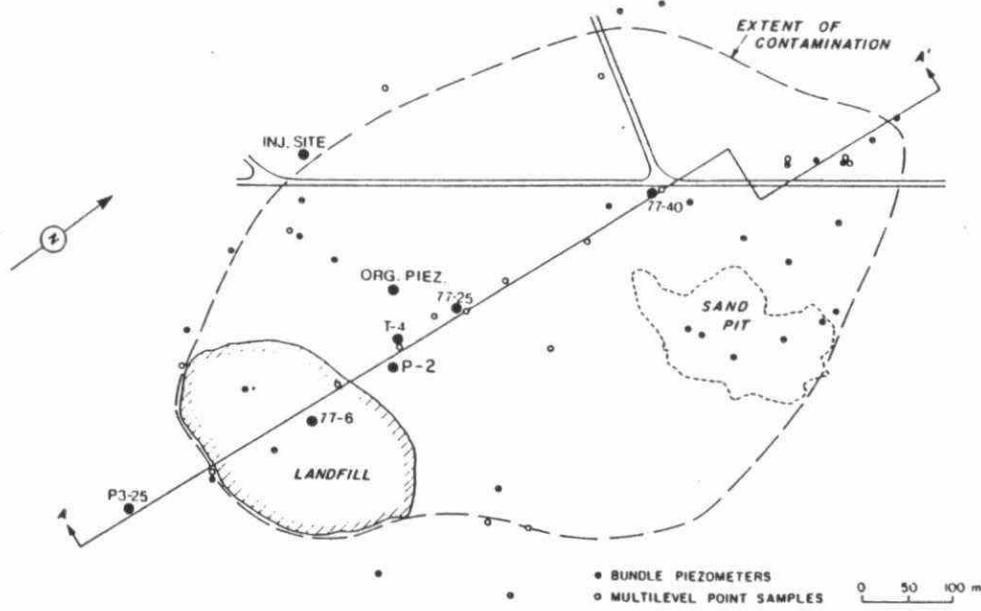


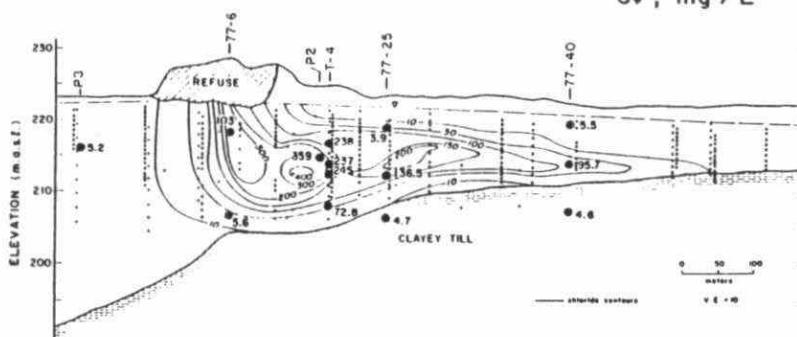
Figure 2. The Borden landfill site, the lateral extent of leachate and the locations of sampled wells and cross-section AA'.

MacFarlane et al. (1983) summarize the hydrogeological studies at this site. Various methods yielded hydraulic conductivities for the aquifer sand in the range of $3 \cdot 10^{-6}$ m/s to 10^{-4} m/s. Based on the representative hydraulic gradient and porosity (0.35), and calculated via Darcy's law, the average horizontal component of the linear groundwater velocity ranges from 8 to 28 m/yr. The plume front would then be estimated to have moved between 300 and 1060 m from 1940 to 1979, a range that brackets the observed plume front movement of almost 700 m by 1979.

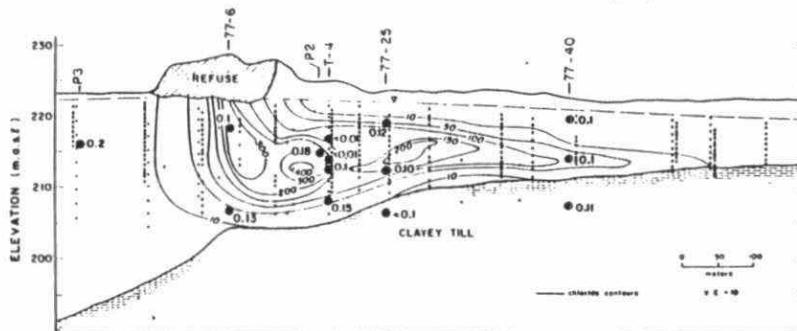
Numerous piezometers were sampled for chloride concentration determination in 1979 and the results for piezometers along cross-section AA' (see Figure 2) are contoured and displayed in Figure 3. Groundwaters from selected piezometers were sampled and analyzed for volatile and extractable organics plus chloride and total organic carbon (TOC) in 1981. Sampling methods and analyses are described by Reinhard et al. (1984). Organic analyses were by gas chromatography following pentane extraction for volatiles and by gas chromatography/mass spectrometry for base/neutral and acid extractable compounds. Analyses were performed by M. Reinhard at Stanford University.

The results are presented in Tables 2 and 3. Concentrations of chloride and selected volatile organics have also been superimposed on the 1979 chloride distributions in the AA' cross-section in Figure 3 so that the data from Tables 2 and 3 can be viewed in terms of their approximate location within the leachate plume.

Cl, mg / L



CCl_4 , $\mu\text{g/L}$



C_2HCl_3 , $\mu g/L$

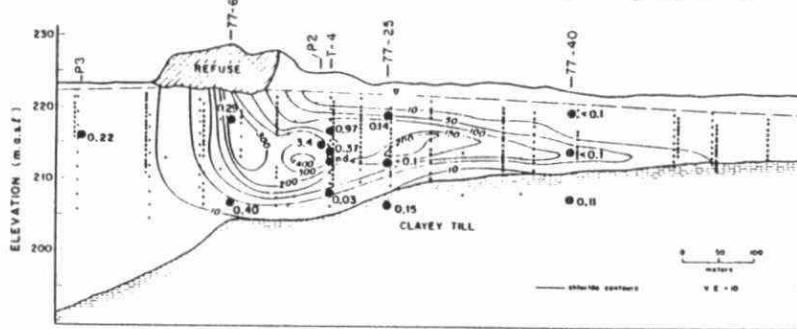


Figure 3. Chloride and selected organic concentrations along cross-section AA' at the Borden landfill site.

Table 2. Chloride, TOC and Volatile Halocarbon Distributions - Borden Plume, 1/11/81.

Piezometer (depth, m)	Cl mg/L	TOC mg/L	CHCl ₃ ug/L	CCl ₄ ug/L	C ₂ HCl ₃ ug/L	C ₂ Cl ₄ ug/L
P3-25 (7.2)	5.2	9.1	<0.1	0.20	0.22	n.d.
77-6 (10.0)	103	43	<0.1	0.10	0.29	n.d.
77-6 (20.7)	5.6	-	<0.1	0.13	0.40	n.d.
P2 (10.1)	359	18.7	<0.1	0.18	3.4	n.d.
T-4 (8.5)	238	-	n.d.	<0.01	0.97	n.d.
T-4 (11.5)	237	-	n.d.	<0.01	0.37	n.d.
T-4 (13.1)	245	-	n.d.	0.1	n.d.	n.d.
T-4 (17.7)	72.8	-	n.d.	0.15	0.03	n.d.
Org. p.z. (5.4)	260	16.0	<0.1	0.18	n.d.	<0.1
77-25 (4.6)	3.9	6.4	<0.1	0.12	0.14	n.d.
77-25 (11.5)	136.5	15.1	<0.1	0.10	<0.1	n.d.
77-25 (16.9)	4.7	-	n.d.	<0.1	0.15	n.d.
77-40 (3.1)	5.5	-	<0.1	0.1	<0.1	n.d.
77-40 (8.5)	95.7	14.3	<0.1	0.1	<0.1	n.d.
77-40 (16.2)	4.6	-	<0.1	0.11	0.11	n.d.
Inj. Site (4.8)	5.6	2.1	0.22	0.25	<0.1	<0.1

nd : not detected

<0.1: trace, below 0.1 ug/L

- : not analyzed

Table 3. Neutral and Acidic Compounds in Groundwaters at the Borden Landfill Site.

(Concentrations in ug/l)

WELL DEPTH (m)	P3-25 7.2	77-6 10.0	P2 10.1	Org.P.z. 5.4	77-25 11.5	77-25 4.6	77-40 8.5	Inj.Site 4.8
<u>Aromatic Hydrocarbons</u>								
Benzene	0.8	2.6(n)	2.8(n)	1.0	0.75	1.7(n)	0.8(n)	1.2(n)
Toluene	0.3	<0.2	0.3(n)	0.8	0.9	1.0(n)	0.7(n)	<0.1
Ethylbenzene	<0.2	<0.2	<0.2	<0.2	0.3	0.3(n)	0.2(n)	n.d.
p+m-Xylene	<0.2	<0.2	<0.2	0.3	<0.2	0.5(n)	0.4(n)	<0.2
Anthracene (Phenanthrene 3)	0.2	0.1	n.d.	0.1	n.d.	0.3	<0.1	0.2
<u>Miscellaneous</u>								
Triphenylphosphate*	n.a.	0.1	n.d.	n.d.	0.4	0.3	<0.1	0.3
Di-ethyl-phthalate*	8.1	2.7	0.5	2.7	12.3	4.8	0.7	6.7
Benzothiazole*	n.d.	n.d.	n.d.	n.d.	n.d.	0.7	n.d.	n.d.
Sulfur (S _n)*	n.d.	>100	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
<u>Acids</u>								
Palmitic*	n.a.	2.3	6.6	13.4	7.2	2.9	6.7	3.2
Stearic*	n.a.	0.8	3.9	6.3	2.3	0.9	2.1	1.2
Linoleate*	n.a.	0.1	0.7	2.5	0.2	0.2	0.2	0.3

n.a. : not analyzed

n.d. : not detected

(n) : average of duplicate analyses

*Semi-quantified as internal standard (no response factor)

Discussion

There is general agreement of the 1981 chloride data with the 1979 chloride distribution (Figure 3). This suggests there has not been a major change in the landfill leachate plume and that the 1979 chloride distribution provides an adequate basis for relating 1981 organics data to the leachate plume.

The concentrations of selected volatile, chlorinated hydrocarbons are only rarely elevated above their concentrations in the upgradient piezometer P3-25 which is taken to be representative of natural groundwater in this area. The exceptions are trichloroethylene (C_2HCl_3) in piezometer P2 and in piezometer T-4 (8.5 m and 11.5 m depth). This indicates the substantial lack of such chlorinated organics in the landfill leachate. These sorts of organics are commonly found in 1 to 100 ug/L concentrations in most municipal landfill leachates (Reinhard et al., 1984; Barker, 1987; Pankow et al., 1986; Cline and Viste, 1985). Similarly, the aromatic hydrocarbons and "miscellaneous" compounds listed in Table 3 show little increase in leachate compared to background groundwater from P3-25. Typically only benzene and elemental sulphur (S_e) are significantly higher in some leachate-impacted groundwaters when compared to the background groundwater.

Unfortunately, groundwater upgradient from the landfill (P3-25) was not analyzed for organic acids. We can assume, however, that groundwater from the "Injection Site" piezometer is not impacted by leachate since it appears to be outside the interpolated leachate plume margin (Figure 2). Using this groundwater as background, it would appear that leachate-impacted groundwaters are sometimes higher in

organic acids than natural groundwaters. This elevation is not unexpected, given the often high organic acid concentrations in municipal landfill leachates (Barker et al., 1987; Reinhard et al., 1984; Chian and DeWalle, 1977). It is perhaps more noteworthy that the organic acids are only slightly elevated in leachate-impacted groundwaters at the Borden site.

Why is the impact of organics from the landfill so slight at the Borden site? The age of the landfilled material could be a factor. Most of the material was probably landfilled before 1950 (MacFarlane et al., 1983) and so before the use of chlorinated hydrocarbon compounds became widespread. Also, the refuse at the Borden site was periodically burned prior to 1973. This could have removed most of the volatile, chlorinated organics and the BTEX aromatics. It could have removed the precursors for the organic acids which are commonly formed by microbial degradation of landfilled organic matter. The practice of burning, perhaps augmented by the lack of chlorinated organics in much of the material landfilled prior to 1950, is likely the major reason for such a low impact of leachate organics upon groundwaters at the Borden site.

THE NEW BORDEN LANDFILL

Site Hydrogeology

In 1976, a new landfill began operation at Canadian Forces Base Borden, on a moderately sloping site, underlain by silty sand till. The New Borden landfill has three equally spaced cells, 60 m by 150 m, formed in excavations between 2 m and 5 m below grade and built up to 8 m to 10 m above grade. The first cell was completed in 1979 and the second cell in 1984.

The stratigraphy of the site is described by Barker et al. (1987) (Appendix C-1). The most important zone hydrogeologically is a silty sand till, in which the base of each landfill cell is located. This sand till is fractured in the top 1 m to 2 m, and is overlain by sand or by a fractured silty clay till. Downward groundwater flow is restricted by a basal clayey silt till.

A well developed contaminant plume, mapped using DOC and Cl concentrations from up to 95 piezometers has been produced by the first two landfill cells. The plume has extended approximately 200 m in the 8 years since landfilling operations were begun, with the main direction of development following the original northward groundwater flow pattern. Infiltration of leachate-contaminated surface waters may also have contributed to the contamination of some shallow groundwater north of the landfill cells.

Hydraulic conductivities that resulted from field tests in the silty sand till ranged from $2.3 \times 10^{-6} \text{ cm s}^{-1}$ to $1.8 \times 10^{-6} \text{ cm s}^{-1}$. Analysis based on the grain-size distribution of the silty sand till resulted in average hydraulic conductivities of $8.1 \times 10^{-6} \text{ cm s}^{-1}$ and $1.5 \times 10^{-6} \text{ cm s}^{-1}$, while laboratory permeameter tests produced values of $2.3 \times 10^{-6} \text{ cm s}^{-1}$ and $1.1 \times 10^{-6} \text{ cm s}^{-1}$. Previous work reported values $1.1 \times 10^{-6} \text{ cm s}^{-1}$ to $5.9 \times 10^{-6} \text{ cm s}^{-1}$. Combining all the various values results in an average hydraulic conductivity of $5.0 \times 10^{-6} \text{ cm s}^{-1}$ for the silty sand till.

Sampling and Analyses of Organic contaminants

Following some preliminary sampling in 1984, groundwaters at the New Borden landfill site were sampled on three occasions in 1985 (05

June, 02 July and 20 August) and again in the summer of 1987. Where the piezometric surface was within about 7 metres of the surface, a peristaltic pump was used to sample the PVC piezometers. After removal of the standing water and sufficient recharge of the well (1 to 12 h), groundwater was drawn via teflon tubing and a short length of silicon tubing in the pumps. Other wells were sampled with an all-metal bailer or with the all-teflon Waterra pump. Samples for volatile organics were collected in organic-free 80 cm³ hypovials without headspace, about 0.2 cm³ of 10% sodium azide bactericide was added and a teflon-faced silicon septum was crimped securely onto the hypovial. One-litre samples were collected from two wells for extractable organic analyses.

One-litre samples were solvent extracted with dichloromethane under acidic and basic conditions and the extract reduced in volume using methods similar to those described by Reinhard et al. (1984) and Patrick et al. (1985). An aliquot was injected onto a HP5890 gas chromatograph coupled to a HP5970 mass selective detector. The mass spectra of all significant peaks were compared to the mass spectra of organics in both the full NBS Mass Spectral Library and the EPA organic priority pollutant subset library. Match qualities in excess of 8000 (80% of perfect match) were generally considered adequate for tentative compound identification, but some judgement was used in assigning identification.

Samples collected for volatile halocarbon and volatile aromatic hydrocarbon analyses were solvent extracted in the hypovials with pentane or hexane and an aliquot of the solvent analyzed by gas chromatography. Peak identifications and peak purity was occasionally monitored by GC/MS analysis with an identical column. Methods are described in Reinhard et al. (1984).

The major organics tentatively identified in contaminated groundwater for piezometers M-7 and B84-1 are listed in Table 4. Various fatty acids were the dominant organics identified. Other than in the volatile class, no EPA priority organic pollutants were identified (phenol, at less than 10 ppb excepted). Consequently, studies at the New Borden landfill site concentrated upon the volatile halocarbons and aromatics.

The spatial distributions of the indicator parameter Cl and selected organic contaminants are illustrated in Figures 4 and 5. These Figures show, in plan view, the maximum concentrations found in 1985 of Cl, carbon tetrachloride (CCl_4) trichloroethylene (TCEY), toluene (TOL) and ethylbenzene (EBENZ). other organics are considered by Barker et al. (1987). These diagrams must be viewed with caution since the three-dimensional aspect of the plumes is not necessarily accurately represented.

The Cl plot outlines the probable extent of leachate impact, although it is not clear whether the 10 or 50 mg L^{-1} contour divides background from impacted groundwater. Sampling was concentrated upon the older cells and so the western portion of the network has received little attention. It is evident that the groundwater contamination extends at least 150 m northward in the direction of regional groundwater flow. The low-level contamination to the west and south of the cells is not likely, hydrogeologically, to have been derived from the waste disposal cells. It could be an artifact of high background values in groundwaters or could be the result of other contaminant sources in this area.

CCL4 was detected ($>0.1 \text{ ug L}^{-1}$) in almost all wells at least once. The low concentration values ($<1 \text{ ug L}$) are probably the result of minor contamination from the PVC wells, from sampling equipment or from laboratory contamination. The distribution of TCEY is more restricted. Concentrations decrease from 750 ug L^{-1} in leachate within the wastes of cell 1 to less than 1 ug L^{-1} within 50 m of the cells. This suggests that the combined processes of dispersion, retardation and biodegradation are limiting TCEY migration. Theoretically, TCEY is slightly less mobile (more highly sorbed and therefore retarded) than CCL4 in aquifers. This is consistent with the more-limited plume of TCEY compared to CCL4. The concentration reduction of TCEY appears to be much greater than for CCL4, suggesting more rapid attenuation of TCEY in contaminated groundwaters.

Table 4. New Borden Landfill Leachate Plume Organics Tentatively Identified by GC/MS Bracketed Values are Estimated Concentrations as ug L⁻¹.

Volatiles

Halocarbons

chloroform (25)
1,1,1-trichloroethane (12)
carbon tetrachloride (4)
trichloroethylene (22)
tetrachloroethylene (0.2)

Aromatic Hydrocarbons

benzene (25)
toluene (1390)
chlorobenzene (2.1)
ethylbenzene (50)
p/m-xylene (119)
o-xylene (58)
cumene (40)
1,2,4-trimethylbenzene (20)
naphthalene (144)

Phenols and Acids

phenol
4-methylphenol
benzenoacetic acid
acid

C₆ to C₁₈ fatty acids and various isomers or methyl esters

Base/Neutrals

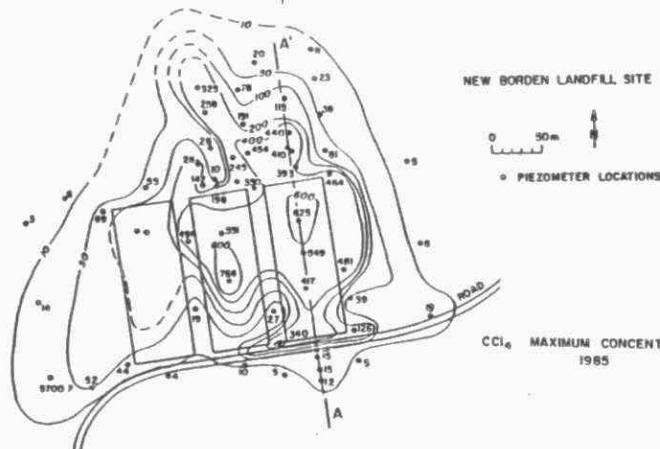
2-hexanone
2-hexanol
d-fenchone

camphor
menthol
3-cyclohexanomethanol
1-isopropyl-4-methyl-cyclohexanol

2-methyl-cyclopentanol
4-propoxy phenol
dimethyl ester of phosphoric acid

N,N-diethyl-benzamide
1,2-benzenedicarboxylic acid, diethyl (?) ester

Cl MAXIMUM CONCENTRATIONS
1985



MAXIMUM TCEY 1985

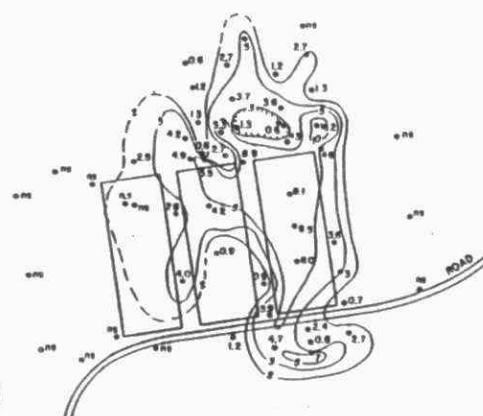
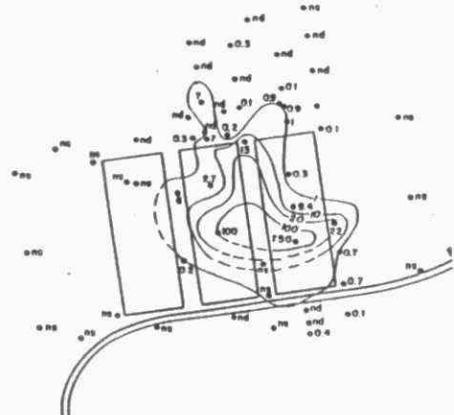
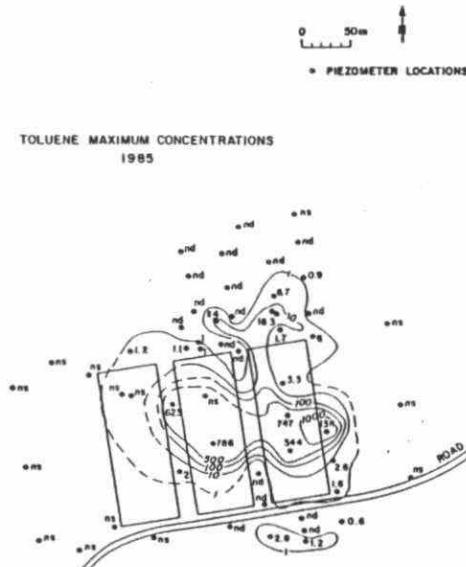


Figure 4. The lateral distributions of maximum concentrations of chloride, carbon tetrachloride and trichloroethylene at the New Borden landfill site.

NEW BORDEN LANDFILL SITE

21



ETHYL BENZENE MAXIMUM CONCENTRATIONS
1985



Figure 5. The lateral distributions of maximum concentrations of toluene and ethylbenzene.

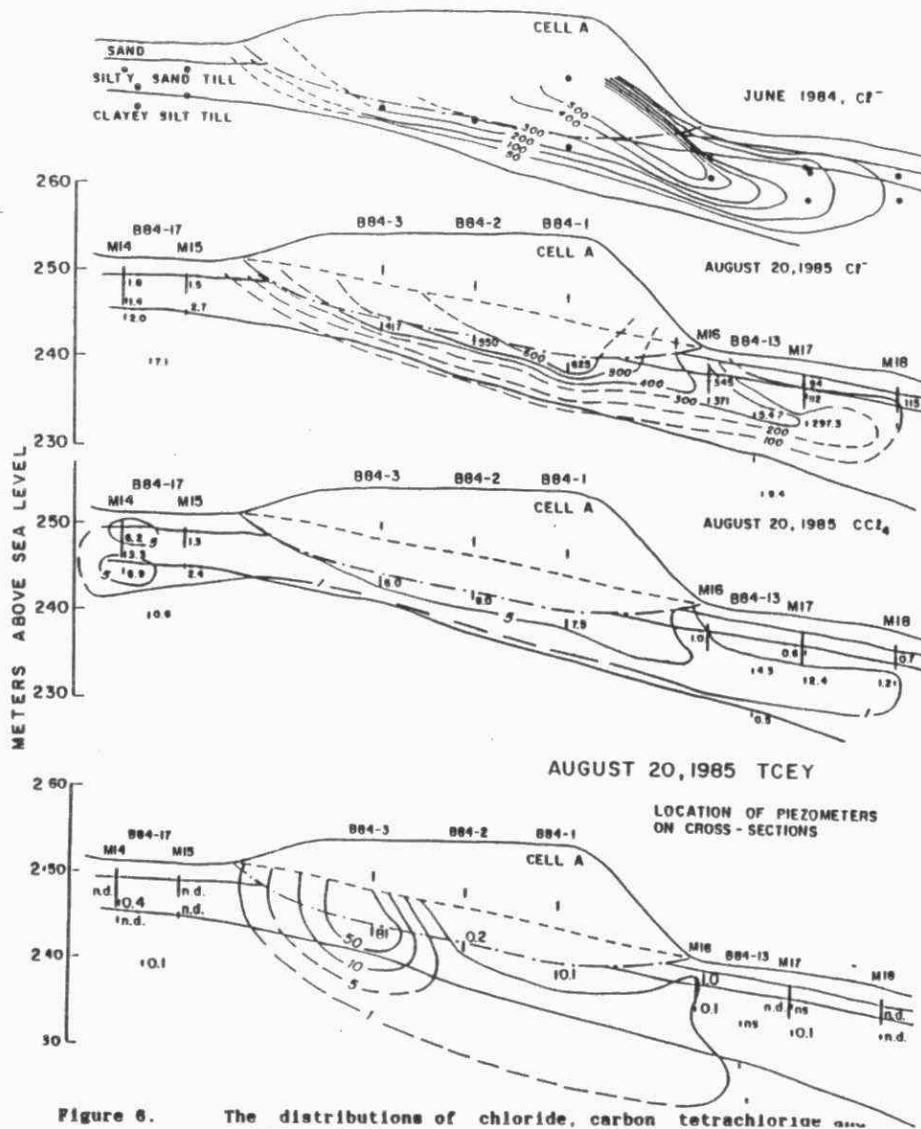


Figure 6. The distributions of chloride, carbon tetrachloride and trichloroethylene in cross-section AA' at the New Borden landfill site.

Ethylbenzene (EBENZ) is widely distributed at low concentrations at this site (Figure 5). This could reflect the occurrence of <1 ug L⁻¹ ethylbenzene in background groundwaters since ethylbenzene is a naturally-occurring organic compound. It could also reflect the pervasive transport of ethylbenzene throughout the plume with concentration reduction due mainly to dispersive processes which are also responsible for reductions in Cl concentrations (Figure 4). Toluene (TOL) shows a more-restricted distribution than ethylbenzene. This difference is not due to enhanced sorptive retardation of toluene since toluene is less retarded in aquifers than ethylbenzene. On the other hand, toluene is more easily biodegraded than ethylbenzene, at least under aerobic conditions. Thus, the restricted migration of toluene likely reflects its more-rapid biodegradation during transport.

Figures 6 and 7 shows the distribution of chloride (June, 1984 and August, 1985) and selected volatile organics in groundwaters sampled in cross-section AA' through the oldest landfill (see Figure 4) cell. The underlying clayey silt till was found to be less permeable than the silty sand till and so the cross-sections were contoured on the assumption that contaminants would migrate in the sand till.

The shape of the Cl plume (Figure 6) has not changed much from 1984 to 1985 except that the 100 mg L⁻¹ contour has extended from M17 to M18 - a distance of about 35 m.

The carbon tetrachloride (CCL4) plume is more extensive than the trichloroethylene (TCEY) plume (Figure 6). TCEY shows the greater concentration decline along cross-section AA'. This is interpreted as greater biodegradation of TCEY compared to CCL4.

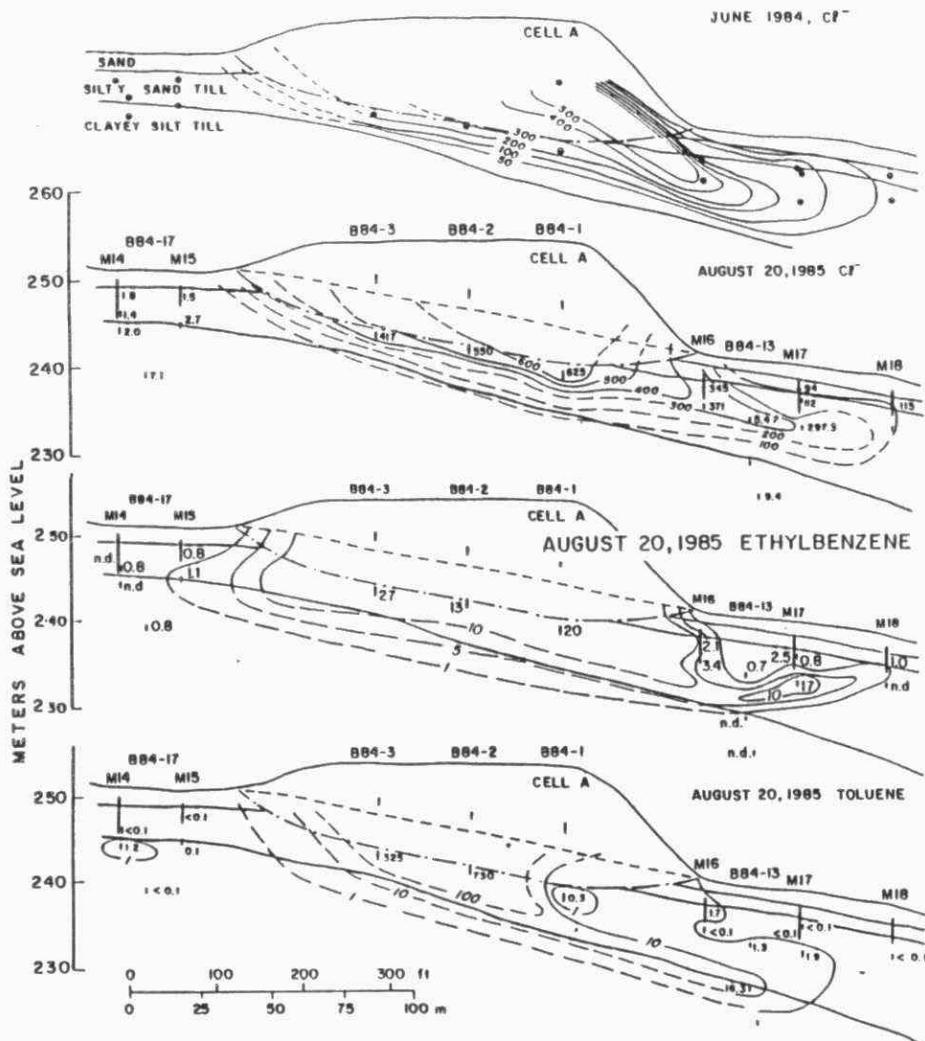


Figure 7. The distributions of toluene and ethylbenzene in cross-section AA' at the New Borden landfill site.

The toluene and ethylbenzene distributions along cross-section AA' are also shown in Figure 7. The toluene (TOL) plume is more restricted in the sand till. The restriction of the organic contaminants is likely due mainly to biodegradation. Sorptive retardation alone is not the controlling process because species such as ethylbenzene and carbon tetrachloride have migrated essentially as far as chloride. It appears that biodegradation must also have occurred, with the restriction of more-mobile organics, such as trichloroethylene and toluene, due to their preferred biodegradation within the leachate plume. Unfortunately, the uncertainty about inputs from the landfill and specific flow paths precludes a quantitative treatment of such processes.

In summary then, very few hazardous organics were found in leachate at the New Borden landfill site. Most organics of concern are either volatile halocarbons or volatile aromatics. Leachate appears to have migrated at least 150 m north from the oldest landfill cell which was operated from 1976 to 1979. Some trace organics also appear to have migrated this far, particularly carbon tetrachloride and perhaps ethylbenzene. Other volatile organics show a migration probably restricted by their biodegradation.

These observations and the interpreted biodegradation are consistent with an anaerobic leachate plume environment perhaps becoming aerobic near the plume limits. Extremely reduced methanogenic conditions probably only occur within the landfill. Less-reduced but anaerobic conditions seem to have permitted the persistence of aromatics and some halocarbons off site. Generally, leachate plume conditions

have not become aerobic however, because aerobic-degradable aromatics persist throughout much of the plume.

SOME COMPARISONS OF THE BORDEN AND NEW BORDEN LANDFILL SITES

Although the inorganic load from the older Borden site is still as high as that from the New Borden site, the general impact of organic contaminants upon groundwaters at the Borden site is less than at the New Borden site. This must reflect differences in the age of the landfill, in the nature of the landfilled material and in the operation of the landfill. Older wastes in the Borden landfill probably contained and produced less halocarbons and aromatic hydrocarbons than are being generated at the New Borden site. Burning of refuse at the Borden site also contributed to the general lack of organics in the leachate. Organic acid generation may have greatly decreased at the older Borden site, while such generation is still high at the New Borden site.

A conclusion that organics present in leachate from present landfills such as the New Borden site will evolve towards the lower concentrations found at the Borden site is probably not warranted. These two sites received different wastes and landfilling practices were very different.

Although the leachate plume at the New Borden site is less extensive than that at the Borden site, it has much higher concentrations of volatile halocarbons and aromatics. The New Borden plume is apparently still expanding while that at the abandoned Borden landfill may be approaching a steady-state. This steady-state indicates a balance has been reached between inputs from the landfill and dispersive dilution within the aquifer. If or when the New Borden plume

reaches a steady-state, it will be interesting to compare the distribution of organics to a conservative indicator such as chloride. In this paper it has been suggested that biodegradation is already limiting the spread or rate of spread of certain organics. If this is true, then the "steady-state" extent of such organics should be much more restricted than that for chloride. This hypothesis could not be tested at the abandoned Borden site because of the very low concentrations of organic contaminants in the contaminated groundwater.

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NATURE OF SUBSTRATES IN INDUSTRIAL WASTES RELATIVE TO ELEMENTAL LEACHABILITY: SEQUENTIAL EXTRACTIONS AND ELUTIONS

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ABSTRACT

Comparison of results of a sequential extraction method under toxic and anoxic (nitrogen) conditions gives similar results for trace metal mobilization except in certain iron-rich matrices where the metals are sorbed to the Fe. Thus the association of trace metal and substrate is important to the mobilization of metals.

The first two steps of the extraction (ion exchange and weak acid) are compared to the MOE leachate extraction procedure (LEP). In most cases, the two steps of the sequential extraction procedure mobilizes more trace metal. Repeatability of the tests is from 1-20% for metals in elevated concentrations (>100 mg/kg) and from 10-100% for trace levels (<100 mg/kg).

Wide ranges in the pH of the slurry of the LEP were encountered due to pH buffering of the sediment. A modification of the elutriation test, employing a pH stat system is proposed in order to eliminate large pH variations.

INTRODUCTION

A previous study [1] developed a procedure for the characterization of industrial wastes by emphasizing the mineralogy, bulk composition and sequential extraction of trace metals. This procedure was applied to a wide variety of industrial wastes. The conclusion was that trace metals incorporated in crystalline silicate matrices were not readily mobile, whereas trace metals in oxy-hydroxide or carbonate matrices were readily mobilized under slightly acidic conditions. In addition, fine-grained non-crystalline wastes generally contained easily mobile trace metals which for the most part were associated with iron oxy-hydroxides or organic matter. The first two steps of the sequential extraction--"exchangeable", as determined by dissolution in $M\text{ MgCl}_2$ at pH of 7, and "carbonate bound", as determined by extraction in buffered $M\text{ NaOAc}$ at pH of 5-- were considered the most sensitive in characterization of trace metal mobilization in industrial wastes. These steps, however, were carried out under oxic conditions, and trace metal mobilization under anoxic conditions, common to many waste disposal sites, was not known.

Regulation 309 for Ontario [2] specifies a "leachate extraction procedure" (LEP) by which extraction is carried out at a pH near 5 which is achieved by successive adjustments of a slurry with acetic acid. Concentrations exceeding 100 times those in schedule 4 of Regulation 309 [2] are considered a "toxic waste". The LEP needs to be characterized for different wastes, and results of the LEP need to be compared to other procedures such as the first two steps of the sequential extraction procedure (SE-2). These comparisons are important in order to give credence to the LEP. If the LEP is shown to be deficient, then other assays are needed.

The purpose of this paper is to report upon differences in results obtained on the first two steps of the sequential extraction procedure underoxic conditions (SEO-2) and under anoxic conditions (SEA-2), and to compare the results of the sequential extraction tests to those found for the leachate toxicity test (LEP). In addition, repeatability for the various tests have been ascertained. Quite different industrial wastes were used for the analyses and comparisons.

PROCEDURES

Solid sample handling and storage is an important factor in trace metal mobilization [3]. The nature of the original sample should not be modified by heating, freeze-drying etc, because the mobility of the metals may be altered significantly. Samples used in this study were air-dried at 50°C and then stored in sealed glass containers. Large aggregate samples were gently pulverized to pass a coarse sand screen prior to air-drying and storage.

The analytical procedures consisted first of characterization of waste samples for mineralogy using X-ray diffraction; for bulk chemistry using X-ray fluorescence and flame atomic absorption (FAAS); for surface area by BET; and for individual particle composition by electron microscopic analysis (SEM and TEM) with elemental determinations using EDS with SEM.

Secondly the samples were analyzed for their trace metal mobilities using the first two steps of the Tessier [4] sequential extraction method (SEO-2), by the first two steps of the Tessier sequential analysis under a nitrogen atmosphere (SEA-2), and by elutriation of trace metals at a pH of

5 after adjustment of the slurry over a 24 hr period, as specified in the OME extraction test (LEP). SEA-2 procedure under nitrogen and the LTL procedure are documented in the following paragraphs. SEO-2 procedure has been previously described [1].

Two-step extraction under nitrogen (SEA-2): Step 1- "Ion exchange":

Approximately 50 mL of $MgCl_2$ at pH of 7 was purged for 30 min by bubbling N_2 through the reagent while stirring. 0.8 mL of the purged $MgCl_2$ was added to 0.5 g of powdered sample, and both sample and reagent were purged again with N_2 with frequent agitation. Samples were capped and placed on a wrist-action shaker for 1 hr. They were then centrifuged, the supernatant removed for analysis by FAAS, and the residue was washed with 8 mL of Milli-Q water and again centrifuged. The wash water was discarded.

Step 2- "carbonate bound": 50 mL of M NaOAc (adjusted to pH of 5 with acetic acid) was purged for 30 min with N_2 . 8 mL of the buffered solution was added to the residue from step 1. The sample and reagent were again purged with N_2 for 20 min with frequent agitation. The samples were capped and mixed for 5 hr on a wrist-action shaker. The mixture was centrifuged, the supernatant was removed and stabilized with 0.5 mL of high purity HNO_3 . The sample was later analyzed by FAAS.

Leachate Extraction Procedure (LEP): Fifty (50) grams dry weight of a powdered sample is placed in a one-litre linear polyethylene bottle with 800 mL of Milli-Q (type I) deionized water. Eight bottles at a time were prepared, capped and placed on a rotary tumbler where the bottles were rotated end over end. After one hour a pH measurement was taken while the slurry was mixed; if the pH was greater than 5.2, acetic acid was added to bring the pH to 5.0. Concentrated ACS grade acetic acid, 10 M or 5M concentration were used. Samples bottles were returned to the tumbler, and the pH was measured and adjusted as necessary at 3 hr, 6 hr and 22 hr. After 24 hr, bottles were removed from the extractor, and about 250 mL of liquid was filtered through a 0.45 μm Millipore filter; 2 mL of ultra-pure concentrated HNO_3 was added to the sample. Metal concentrations were measured by FAAS using standard addition techniques and dilution as needed.

A blank was carried through the entire procedure, and the pH's and amount of acetic acid required were logged. These data are used to define

a "buffering stability index" (BSI) of the sample. The BSI is merely the moles of acid required over a 24 hr period to maintain a pH of about 5 per gram of dry solid.

RESULTS

Repeatability of Methods

Both the LEP and the SE methods were examined as to repeatability of results. Samples exhibiting both large and small concentrations were used in replicate analyses. Table I shows the relative standard deviation for steps 1 and 2 of the sequential extraction under oxic and anoxic conditions, and table 2 shows the deviation for the LEP. A range of samples, consisting of industrial chemical waste, brass foundry dust, and iron/steel industry waste were used in the replication study. Replication expressed as standard deviation/mean is poorer for low concentrations than for high concentration, varying up to 200%, but with typical values between 10-100%. This rather poor repeatability is to be expected. High concentrations replication is better with ranges typically less than 50%. Iron has the poorest replication for high concentrations. This may be due to the fine particle sizes not always being efficiently extracted by centrifugation and filtration; in addition, small variations in Eh and pH conditions would affect iron compound solubility and desorption greatly. Considering the 3-5 orders of magnitude variation in concentration of trace metals found in waste samples, the replication of all methods is considered quite acceptable. It is obvious, however, that duplicate analysis of samples with high metal concentrations are warranted to verify results.

Sequential extraction under oxic and anoxic conditions

Seventeen different sample types, consisting of foundry slag, smelter slag, iron/steel dust, brass foundry waste, industrial chemical wastes and municipal waste were analyzed for mobility under oxic and slightly anoxic conditions using the "ion exchange" and "carbonate sediment" steps discussed above. In general differences in results from the two methods were within or very near to replication levels as shown in table I. There also was no significant difference in concentrations in steps 1 and 2 for the oxic and anoxic extractions. It is therefore concluded that the more

Table 1. Repeatability of steps 1 and 2 of the sequential extraction procedure under oxic and anoxic (N_2 atmosphere) conditions. RSD: relative standard deviation. Values in brackets are number of samples run. Units are mg extracted/kg of solid.

Element	Oxic		Anoxic	
	Mean	RSD	Mean	RSD
NI (low)	6-43 (6)	70-100%	6-62 (6)	70-100%
(high)	200-710 (4)	1-40	250-300 (2)	8-50
Cd (low)	1-10 (6)	0-200%	1-8 (6)	0-100%
(high)	1450-16,200 (2)	4-9	1590-16,500 (2)	10-13
Cu (low)	22-230 (9)	2-80%	24-150 (7)	6-100%
(high)	450-125,000 (5)	4-27	450-42,000 (7)	10-68
Pb (low)	14-130 (10)	4-19%	15-120 (10)	1-50%
(high)	3000-44,000 (3)	4-20	3300-42,000 (3)	1-16
Zn (low)	60-100 (8)	2-19%	60-100 (8)	15-33%
(high)	3500-55,000 (8)	5-41	2300-47,000 (8)	5-45
Mn (low)	15-65 (10)	0-30%	15-75 (10)	10-55%
(high)	220-550 (6)	5-10	500-600 (6)	15-25
Fe (low)	15-110 (8)	30-200%	9-75 (8)	10-74
(high)	1000-21,000 (8)	10-100	800-15,000 (8)	4-60

Table 2. Repeatability for the leachate extraction procedure (LEP).

Element	Mean	RSD
NI (low)	0.6-80 (6)	4-24%
(high)	190 (2)	7
Cd (low)	0.1-5 (6)	0-100%
(high)	15 (3)	8
Cu (low)	3-190 (4)	33-45%
(high)	4400-7600 (4)	15-40
Pb (low)	20-410 (4)	11-50%
(high)	7500-42,000 (5)	14-28
Zn (low)	10 (2)	10%
(high)	1300-40,000 (7)	2-9
Mn (low)	9-150 (9)	5-60%
Fe (low)	2-1000 (9)	5-85%

difficult and tedious extraction under nitrogen is not justified. Perhaps an extraction under a stronger reducing environment will show differences with the oxic extraction.

The following discussion refers to differences in concentrations obtained for step 1 ($M\text{gCl}_2$) and step 2 (buffered acetate system at pH of 5) for various samples. In most cases, trace metals were not mobilized until the second step, but there are some noteworthy exceptions when significant metal was elutriated by step 1. These exceptions must reflect very mobile metal that is weakly sorbed on the surfaces of the substrates. We found that Cu, Zn, Ni and Cd were the metals mobilized to any degree by step 1. High concentrations in step 1 were found for brass and steel foundry dust, metal refinery residues, smelter dusts, industrial chemical wastes, and a municipal waste. Slags typically did not release metals in step 1 and often to only a small degree in step 2. On the other hand, dusts at the same industrial site often show 2-3 orders of magnitude increase in concentration, often being mobilized in step 1. This finding suggests that the metals are sorbed, perhaps by weak electrostatic bonds on the surfaces of solids. Other correlations between metal mobility and nature of the substrate are:

- Elevated concentration of metals (e.g. > 0.1%) in bulk analyses are good indicators of metal mobility especially for Cu, Cd and Zn, but not for Pb.
- Industrial wastes described as "dusts", typically have greater metal mobility than similar composition slags.
- Metals existing as discrete crystalline compounds as oxy-hydroxides, carbonates and sulfates are generally very mobile, whereas metals associated with silicates are more inert. (These compounds are characterized by powder X-ray diffraction analysis.). A relatively soluble crystalline compound was detected by XRD in all samples which gave a major metal concentration in step 1.

Therefore the easily extractable metals are found in samples with relatively soluble crystalline phases and/or are weakly sorbed on fine-grained surfaces. Work is presently underway to determine if a mineral equilibrium model calculation (e.g. MINEQL) would simulate the metal concentrations, given only the crystalline composition and leaching condition. If this is possible for the more mobile wastes, a powerful

predictive leaching tool would result.

Leachate extraction procedure and comparison to sequential extraction

The LEP procedure requires the continuous adjustment of pH over a 24 hr period. There are major pH drifts to higher pHs after acid adjustment for most samples. This is due to the very strong pH buffering of the sample. In increasing strength, the sediment buffering is due to reaction with silicate minerals, surface exchange (with metal), or dissolution of oxy-hydroxides and carbonates. An operationally defined buffering index (BSI) is defined as:

$$BSI = \frac{\sum A}{W}$$

where $\sum A$ is the total equivalents of acid added and W is the dry weight of sediment (g). The BSI can be zero (or negative) for samples that have an acidic buffer (e.g. some untreated metal plating wastes), is quite small (about 10^{-5} to 10^{-6} eq/g) for coarse grained cohesive silicates (slags), and large for dusts (10^{-3} to 10^{-2}), and maximum for wastes containing carbonates and fine-grained oxides ($> 10^{-2}$). Since acid addition reflects sample reactivity by the release of metal by one or more mechanisms, the actual amount of acid consumed is an indirect indicator of the stability of the metals in the waste.

Reaction rate also varies among different wastes. Silicate based wastes (slags) are pH stabilized in the first or second adjustment of acid, whereas fine grained wastes (dusts) and oxide and carbonate bearing wastes often are not pH stabilized after 24 hr. The longer times required for the latter two types of wastes are probably due to slower reaction rates controlled by surface processes. This reaction rate of selected wastes is being examined using a pH stat set-up in order to better define the metal release - H-Ion uptake mechanisms and to be able to comment upon the appropriateness of stabilizing a sample for 24 hr in the LEP.

All samples analyzed by the selective extraction (2 steps) were also analyzed using the leachate extraction procedure (LEP). In all but one sample type, the two step sequential extraction (either oxic or anoxic) mobilized significantly more trace metals than did the LEP. The differences were greatest for industrial chemical wastes and dusts. For example, the SE method released 4500-4600 mg/kg Cu compared to 327 mg/kg using the LEP for a metal refinery waste; 42,000 mg/kg of Pb were

mobilized using the SE compared to 32,000 and 20,000 mg/kg of Cu using the SE compared to 66 mg/kg using the SE method for a brass foundry dust. On the other hand, 5 different iron/steel and smelter slags gave very similar results.

The results are somewhat surprising because the second step of the SE method should be very similar to the LEP procedure. In addition, the results are extremely important since the LEP is proposed as a prime procedure for assessing metal mobility in wastes. The reason for the lower metal values for the LEP method are hypothesized to be due to re-adsorption on substrates, especially iron/manganese oxides. In all samples showing marked differences in metal release, the Fe and Mn values are very different and very large; whereas in samples showing similar results, the Fe/Mn values are small and similar. If this hypothesis for the differences in mobility is true, the pH adjustment and regulation is the sensitive step in metal mobility.

At present, the LEP method must be considered suspect as being able to actually characterize waste mobilization of metals at a pH near 5. Tests are presently being carried out in a pH stat at 5.2 to determine the rate of metal release and to compare the differences from the pH stat and the LEP procedure.

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**REPORT ON CODISPOSAL OF MUNICIPAL
AND INDUSTRIAL WASTES**

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Introduction

This work concerns the practice of disposal of hazardous solid waste with municipal refuse. Although commonly utilized in Europe, there is little direct information on the impact of the municipal refuse environment on the stability of the disposed solid wastes, nor of the influence of the industrial waste on the municipal refuse decomposition. Field studies do not allow the effect of the interactions to be investigated. However laboratory experiments seldom reflect the conditions found in the field and their use is equally limited. In this work, a method for studying the codisposal operation which would reflect field conditions and allow scientific investigation of the codisposal effects was devised. The experimental apparatus was constructed, tested and then operated. Methods of handling and coping with the variability of: municipal refuse, the required scale of operation to reflect a municipal refuse site, the effect of environmental parameters (precipitation and evaporation), the time scale of the operation (years), sampling, data collection, multielement and species analyses, and data reduction, all had to be incorporated into the study. A total of 16 experimental test cells were constructed and all the cells have passed two winter seasons and are in good operating condition.

This report is a partial summary of the three year study. It is important to note that municipal refuse environments undergo distinct changes with time and that the results presented in this work represent a relatively young landfill.

Objectives of Study

1. to design and construct experimental test cells for the investigation of factors affecting the stability of solids in a municipal refuse environment
2. to investigate the effects of codisposal of hazardous solid wastes on the municipal refuse environment.
3. to develop an information base which will permit the significance of various parameters to be quantified for the development of a model of landfill leachate generation.
4. to investigate the solubilization of contaminants in the municipal refuse leachate as a function of industrial waste loading and atmospheric precipitation.

Current Status

There are 16 experimental test cells in operation. No columns have failed, however there have been some operational upsets. Power supplies have failed twice during the winter periods. Both problems were corrected within a few days (relay contact failure and a transformer failure). A vacuum pump sampler also failed (motor windings corroded). These types of problem are to be expected with equipment operated under environmental conditions.

All materials of construction have held-up, although replacement of the outer aluminium foil sun shield is required every year.

Failure of sampling check valves is a persistent problem that is related to poor manufacturing or quality control. Over 50% of these valves failed in the first year causing some leachate loss. Most of the failures were incorrect assembly and damaged internal seals. Substitution will be carried out as the valves fail. Despite these problems it is anticipated that many of the valves will provide years of useful service.

Data analysis collation and storage has proved to be an onerous task. Data is currently manipulated with the aid of a computer, a PC XT clone. The system has 640 K internal memory and two floppy disk drives. Although the data storage on the floppy disks is satisfactory, data access is cumbersome and with continuing data collection a hard disk drive with 20 Mb capacity will be required. Despite the limitations of a PC computer, this route has proven cost and time effective over main frame use. Ultimately there will be mainframe access from the PC for major data calculation.

Data being stored from the 16 experimental test cells include: moisture input (atmospheric and control), leachate volume, temperature, pH, Eh, COD, ICP analysis (Mn,Fe,S,Be, P,Mg,As,Si,Mo,Pb,Se,Ca,Cu,Sb,Al,Co,V,Zn,Cr,B,Ni,Cd,Ba) and NAA analysis (Br,Mg,Cu,Na,K,Cl,Al,Mn,Ca). With sufficient data to now smooth out the normal variability of this complex system it is apparent that there is a significant effect exerted by the solid industrial waste on the municipal refuse degradation process.

Experimental

A schematic of the experimental test cells are shown in the figure 1. Collection of the leachate, from a bottom drain, is carried out weekly, using syphoning action assisted by the application of a vacuum when required. The system has been maintained in an unsaturated flow condition with regular leachate removal from the bottom reservoir in the test cells. Details of the apparatus and techniques

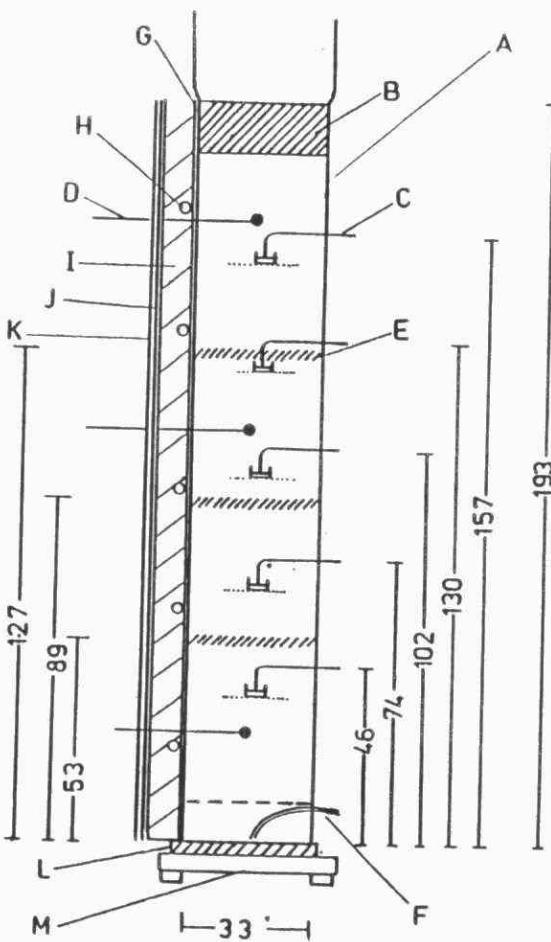


FIGURE 1 Column Schematic

A polyethylene column, B sand layer, C sampling ports
D thermocouples, E industrial waste, F bottom sampler
G aluminum wrap, H heating element, I insulation
J polyethylene wrap, K aluminum wrap, L polyurethane
insulation, M wooden stand, N snow collar.

Dimensions in cm.

have been given in earlier reports.

Since both ICP and NAA analyses have been used, a cross check of the two techniques has been maintained. Good statistical analysis over several hundred measurements has confirmed the linearity of the two methods, but has shown that an element proportionality factor must be used to convert values from one technique to the other. Slight elevation of ICP values by the presence of organics has been implicated in the difference.

COD measurements were added to the routine analyses performed after the first year.

Results

As a consequence of having one half of the experimental test cells open to the environment and the other half enclosed for controlled water addition, a good determination of evapo-transpiration losses could be made. The values refer to a sand covered, not vegetation covered surface. The water loss due to evaporation was very constant ranging from 23% to 27% of moisture input. The test cells having only sand had moisture input losses of $28 \pm 2\%$. Losses from the control columns were $0 \pm 1\%$ apart from extraneous loss due to malfunctioning valves.

The correlation between rainfall measured at the test cell site by a standard rain gauge and meteorological data, was exact. Since the official data is collected relatively close to the test cell site the correlation is to be expected. A digital rain gauge also set up at the site, proved to be unreliable and its use was abandoned.

The behaviour of the test cells with respect to leachate generation and field capacity is shown in figure 2 for municipal refuse only as a function of rainfall. Until breakthrough occurs and leachate is generated, the columns absorb all of the moisture input. This is represented by the 45° line. After breakthrough the slope of the line representing the data indicates the moisture loss due to evaporation. The control columns with little or no evaporation loss display zero slope after breakthrough as seen in figure 3, column #7. An extraneous loss, such as a valve leak results in the vertical displacement of the data as seen in figure 3, column #8. Thus by simple monitoring of leachate volume and moisture input, an accurate measure of the test cells performance can be kept.

Field capacity for the 12 test cells with municipal refuse was reached at 0.72 wt. H₂O per wt. dry solid with a standard deviation of 0.12. The presence of industrial waste in the municipal refuse did not affect the moisture balances of the test columns. The 4 columns with sand had a field capacity value of 0.054 wt. H₂O per wt dry solid with a standard deviation of 0.01.

The moisture input to the control columns is based on an

Fig. 2: Field Capacity determination

Atmospheric Columns

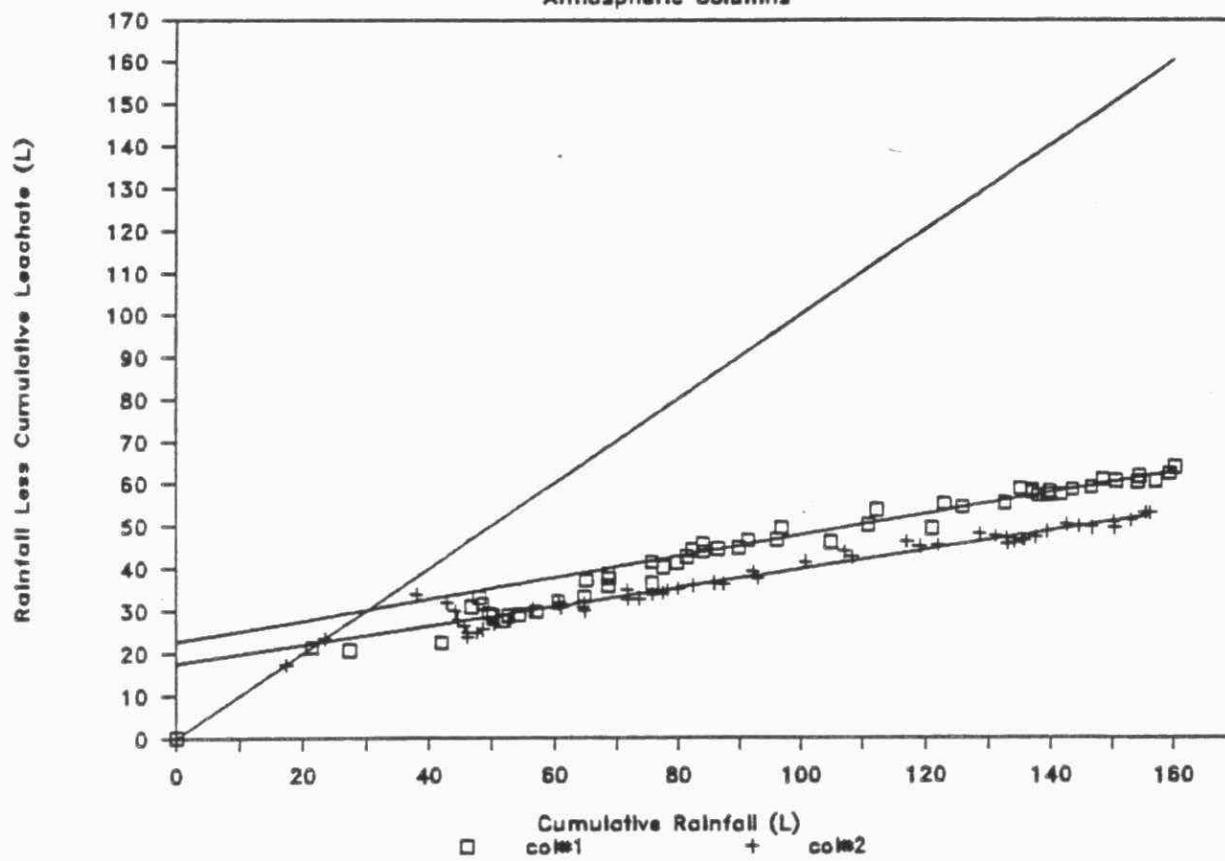
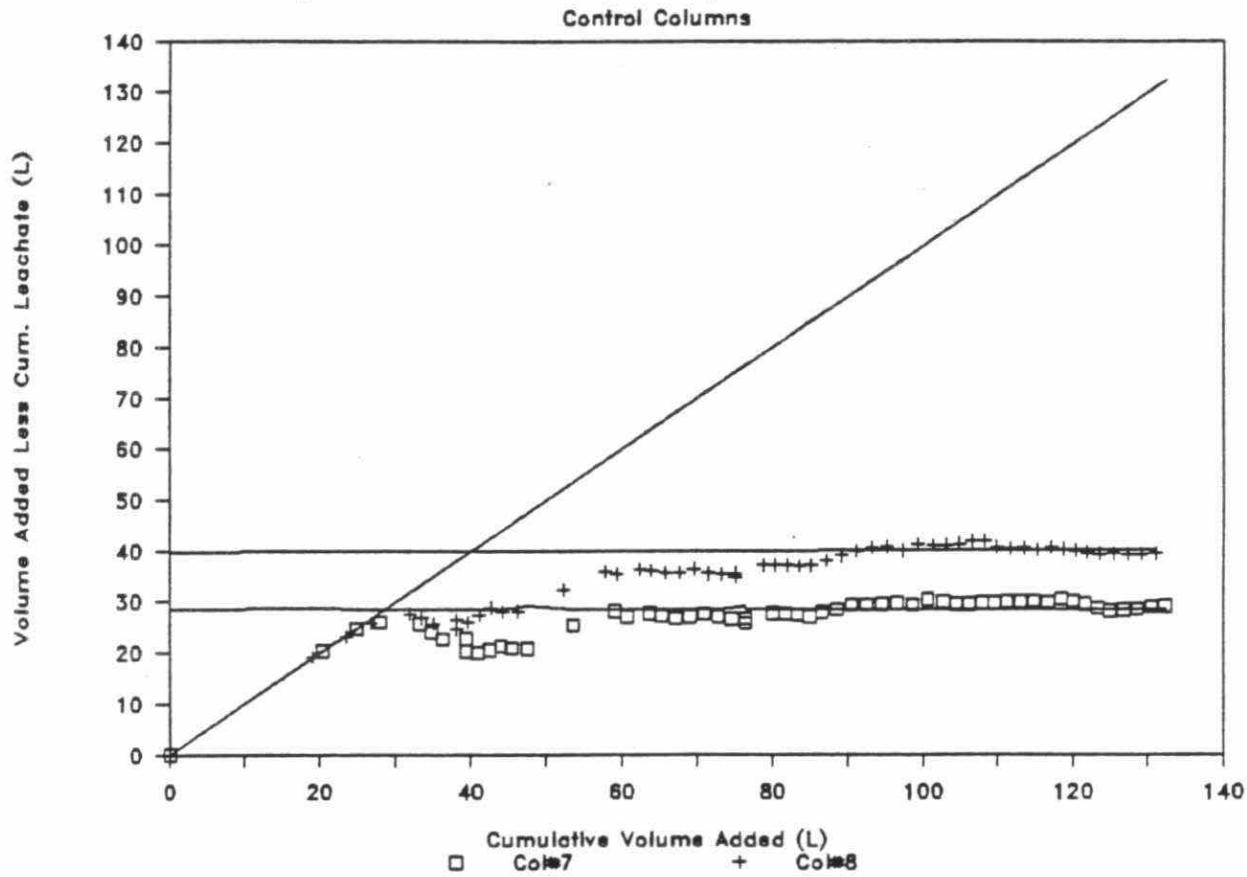


Fig. 3: Field Capacity determination



11 year monthly average without allowance for evaporation and is thus different than the atmospheric precipitation input. In order to report the results of the leachate generation and metal mobilization, the data has been presented on the basis of cumulative leachate volume collected so that a valid comparison of atmospheric and control test cells may be made.

Results of Fe, Cd and Pb concentrations (figures 4a, 5a and 6a) are shown for 4 municipal refuse test cells(100% MW). Two of these cells have controlled moisture and two have atmospheric moisture input. Figures 4b, 5b and 6b have the equivalent information for the 92% MW and 8% IW codisposal test cells. As can be seen from the figures, Fe, Cd and Pb concentrations are depressed and not elevated in the leachates from test cells with industrial waste. Typically all of the heavy elements Fe, Zn, Cd, Mn, Pb, Ca, Mg and S, are depressed in the leachates from the codisposal tests. This suppression is very significant since the industrial waste, a steel flue gas dust, adds a significant burden of metal species to the municipal refuse. The effect is even more dramatic when the total metal leached is shown, for example, iron in figure 7a,b. In this case the total amount of iron discharged in the leachate is reduced by a factor of 2 when codisposal is used. Only in the case of chromium elution does there not appear to be any significant difference between the codisposal and normal test cell results. Results for other elements are provided in the Appendix.

This behaviour of metal ion suppression was not predicted by the EP Leach Test for solid waste nor by the longer (1 month) modified codisposal leach tests that were initially performed.

The suppression effect of metal ion contaminants in the leachates, extends to a minor extent to the alkali metal and halides species. Figures 8a,b and 9a,b show the total amount of potassium leached from MW, MW+8% IW, MW+30% IW and 8%IW in sand. The 8%IW contributes from 4 to 18 g of potassium and the MW contributes from 40 to 60 g of potassium. Thus, based on the respective loading of industrial and municipal wastes, the predicted no interaction values for the codisposal of 8% and 30% IW are 54 and 113 g respectively. The measured values of 51 and 95g can be found from figures 8b and 9a. Both atmospheric and controlled moisture have been averaged. The over-prediction, though small, of the amount of species leached is similar for the ions Na, K, Br and Cl. This behaviour reflects the degree of interaction between the refuse and industrial waste.

To further investigate the suppression of metal contaminants in the leachates from the codisposal test cells, it is useful to correlate the behaviour with the parameters Eh, pH and S.

The effect of 8% industrial waste on the leachate pH is shown in figure 10b. The resultant leachate pH of the 4

Fig.4a Municipal Refuse Only

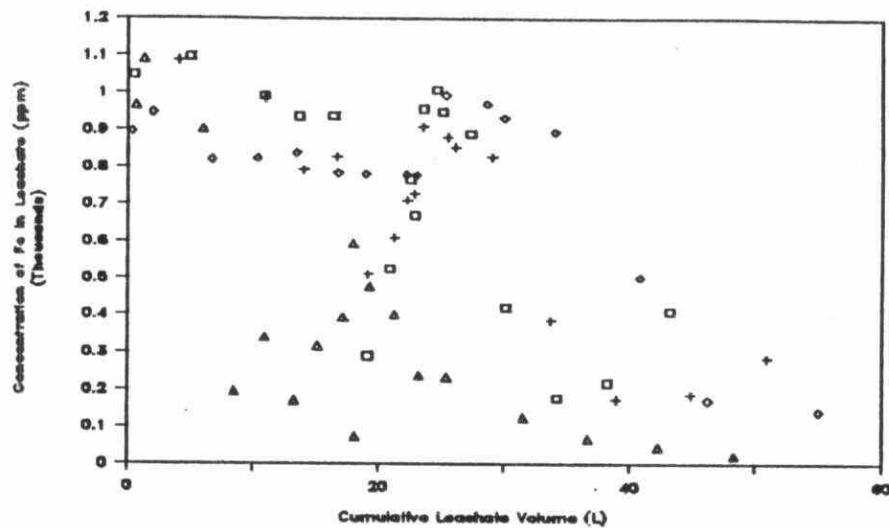


Fig.4b Co-disposal 8% Industrial Waste

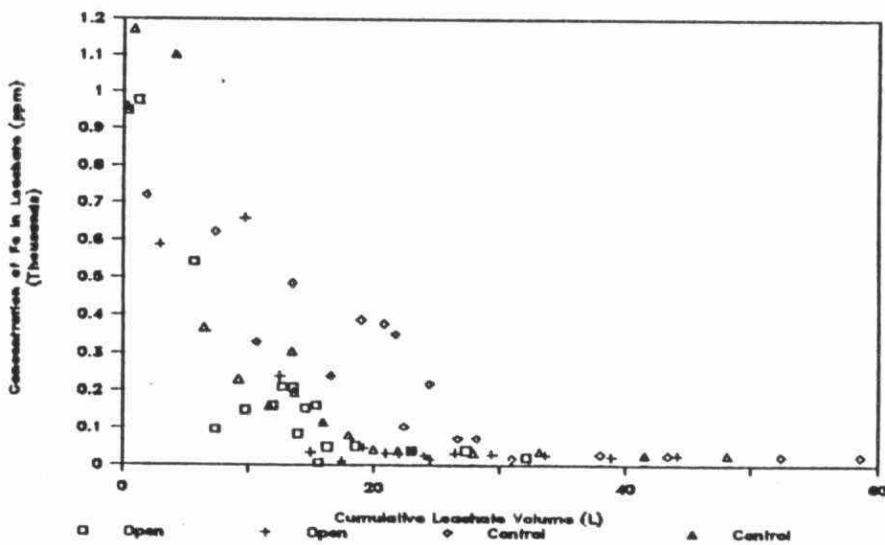


Fig.4a,4b: Effect of Co-disposal on Fe Leached for both open and Control Columns.

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Fig.5a Municipal Refuse Only

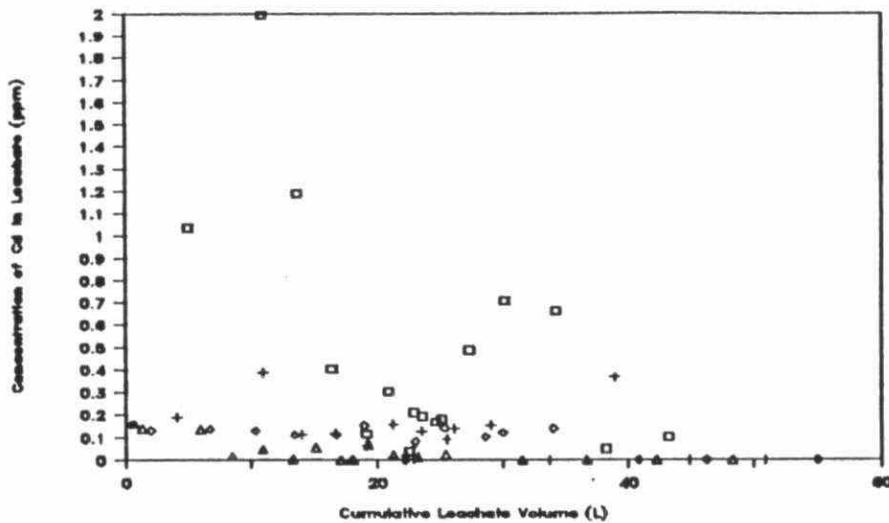


Fig.5b Co-disposal 8% Industrial Waste

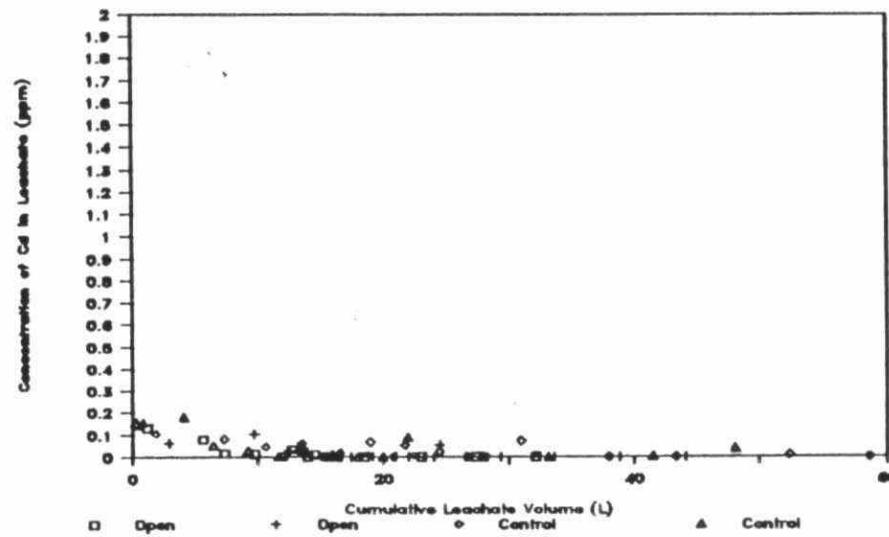


Fig.5a,5b: Effect of Co-disposal on Cd Leached for both open and Control Columns.

Fig.6a Municipal Refuse Only

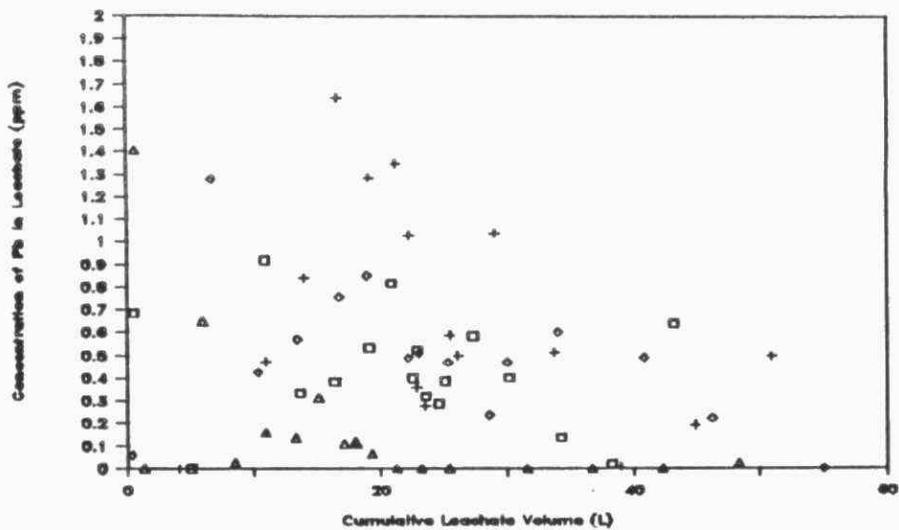


Fig.6b Co-disposal 8% Industrial Waste

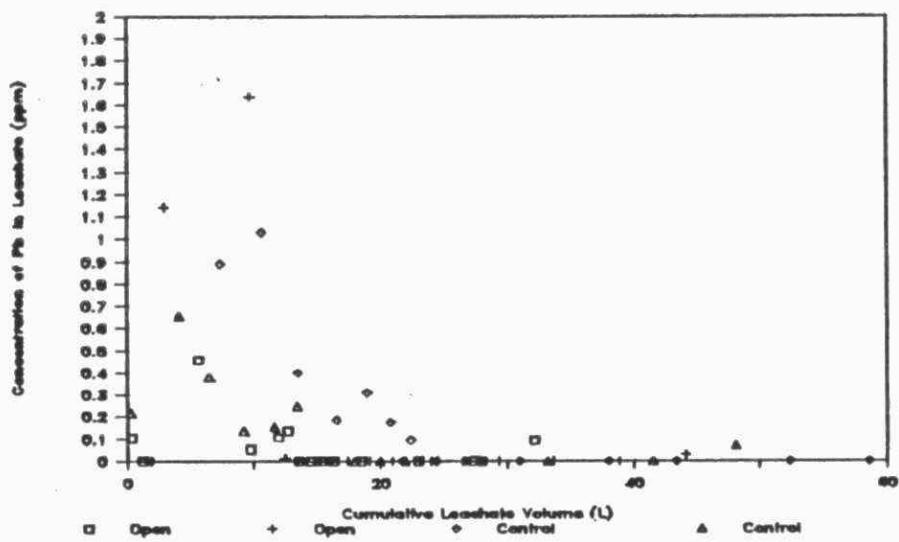


Fig.6a,6b: Effect of Co-disposal on Pb Leached for both open and Control Columns.

Fig.7a Municipal Refuse Only

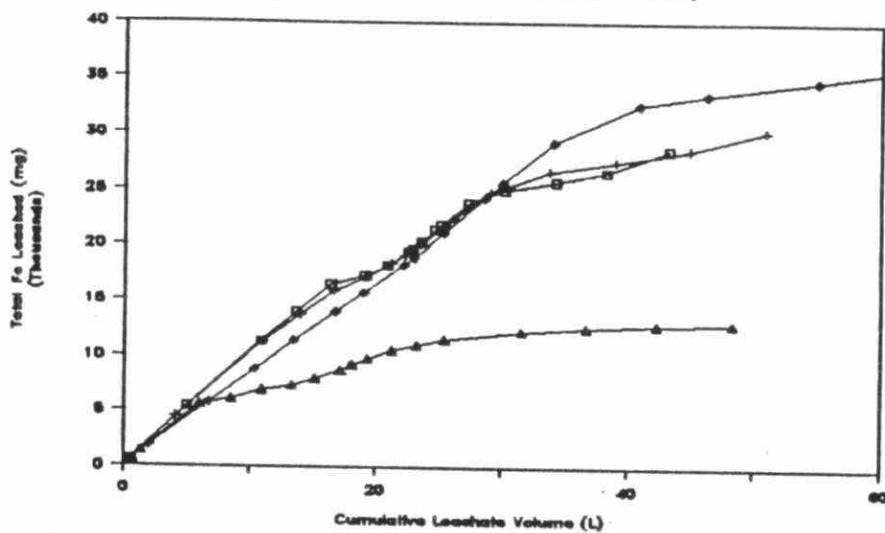


Fig.7b Co-disposal 8% Industrial Waste

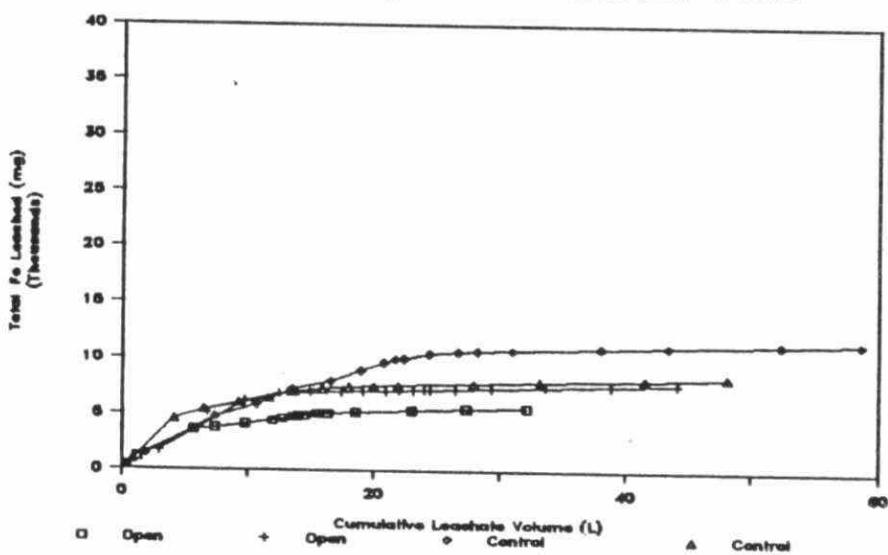


Fig.7a,7b: Effect of Co-disposal on Total amount of Fe Leached for both Open and Control Columns.

Fig.8a Municipal Refuse Only

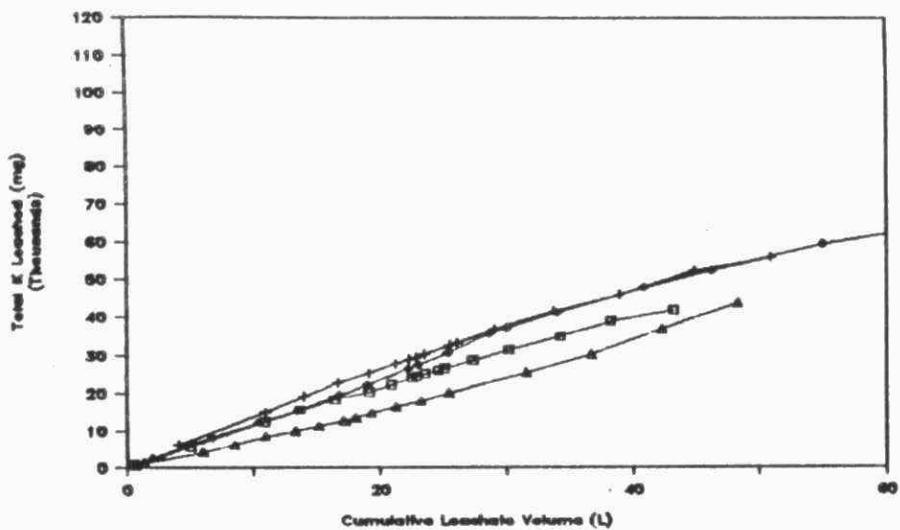


Fig.8b Co-disposal 8% Industrial Waste

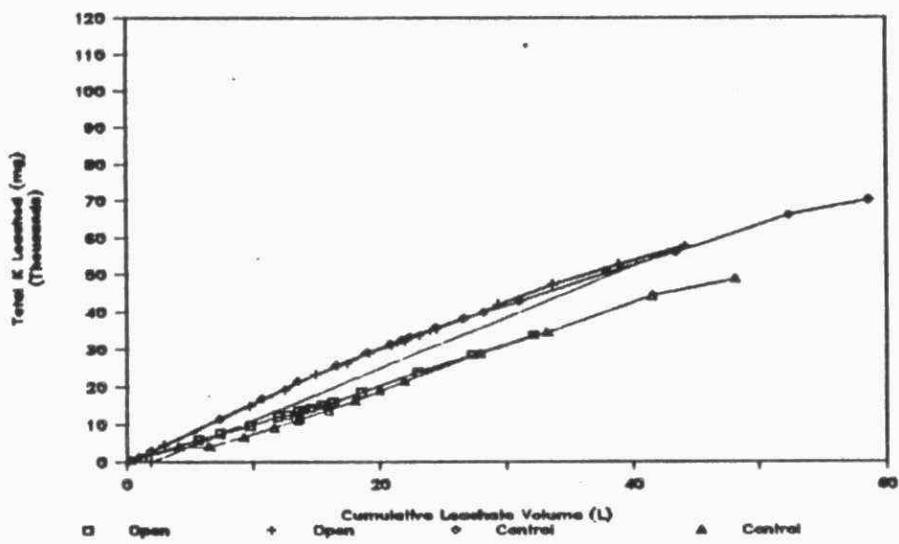


Fig.8a,8b: Total amount of K Leached from Municipal Waste (MW) and Co-disposed MW+8% Industrial Waste.

Fig.9a Co-disposal 30% Industrial Waste

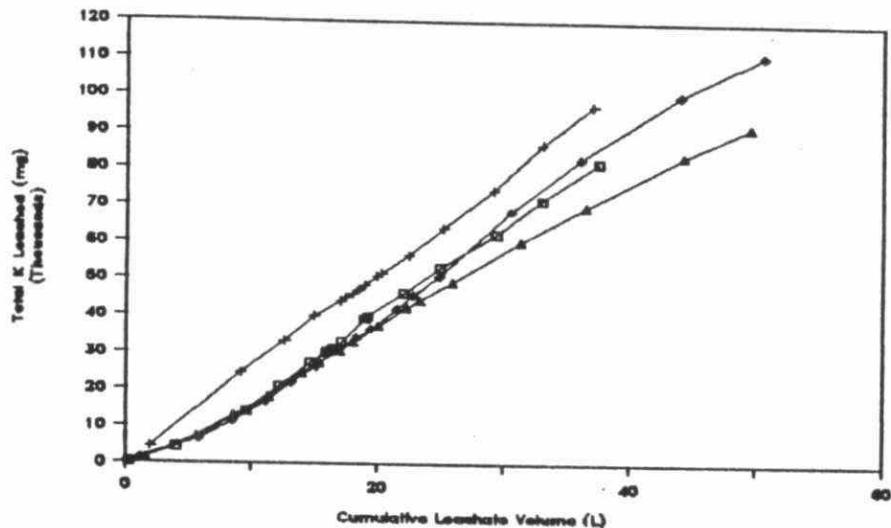


Fig. 9b: 8% Industrial Waste in Sand

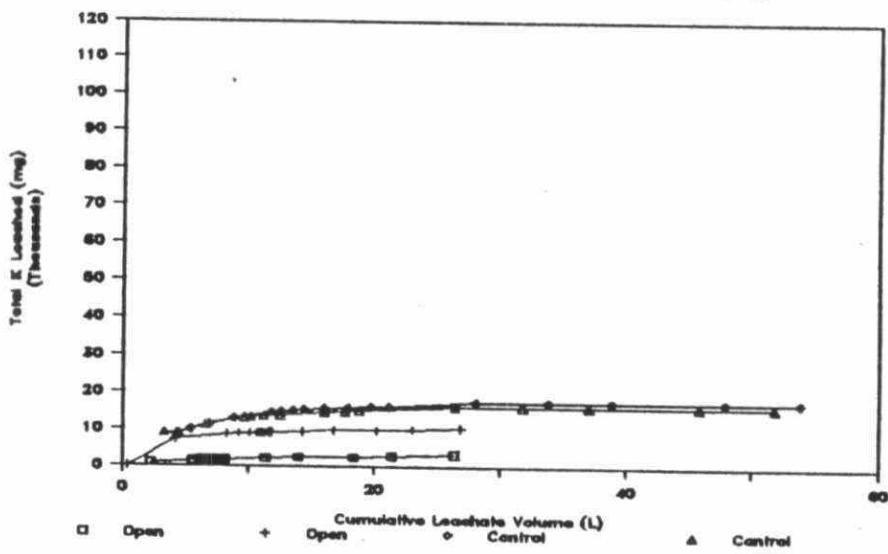


Fig.9a,9b: Total amount of K Leached from Co-disposed MW+30% IW and 8% Industrial Waste in Sand.

municipal refuse only test cells is shown in figure 10a. From these figures, the leachate pH has stabilized at 5.5 for the MW tests and at 7.4 for the MW+8% IW tests. The leachate had initially been buffered at pH= 5.5 in all columns for the first several months as was predicted by the laboratory codisposal EP Test, but this effect was relatively short lived. Although the generation of more alkaline leachate has been reported in the literature, it is incorrect to assume that the presence of the alkaline industrial waste is the sole contributing factor. One of the test cells with only municipal refuse also has displayed this alkaline pH drift (figure 10a) and test cells with 30% IW also have shown both pH levels (figure 11). There is no doubt that the leachate pH is an important factor and may explain some of the observed metal ion suppression. The more alkaline leachates from the experimental test cells have lower concentrations of Fe, Zn, Mn, Pb, Mg, and Cd. Thus the relatively alkaline leachate of the MW test cell (column 4) has relatively low concentrations of Fe, Zn, Mn, Pb, Mg and Cd compared to the other municipal refuse test cells.

The pH value of the leachates is determined by biological activity rather than by direct chemical equilibrium, so that a change in pH also should be reflected by an alteration in the microbial population. Thus measurements of Eh, dissolved oxygen, COD and S should show corresponding changes. Direct Eh measurements are often difficult to interpret since the measurement reflects the relative concentrations of all the oxidizable and reducible species in solution. Although the variability of the Eh measurements was large, the same behaviour that was observed with the pH measurements can be observed. Test cells with more negative Eh values had more suppressed metal concentrations. The correspondence between Eh and pH is demonstrated in figure 12. The regression coefficient is 0.76 where 1.0 would indicate perfect fit. A theoretical model based on the expected behaviour if only dissolved oxygen were involved is plotted as a dashed line in the figure. From this plot it is clear that the dissolved oxygen content appears to play a significant role. A further indicator of the biological activity is the amount of dissolved sulphur. Although of relatively low concentration compared to many of the contaminants, the correlation with pH is consistent with biological activity.

A table shown below demonstrates how the quality of the leachates from the experimental test cells may be associated with various parameters. Columns 1-4 contain only MW, 5-8 contain MW + 8% IW, 9-12 contain MW + 30% IW and 13-16 contain 8% IW in sand.

Fig10a: Municipal Waste Only

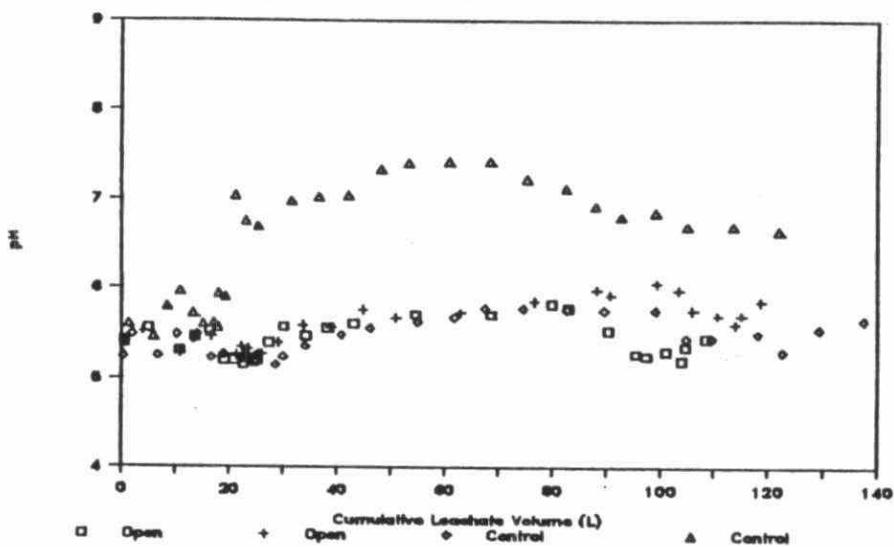


Fig10b: Co-disposal 8% Industrial Waste

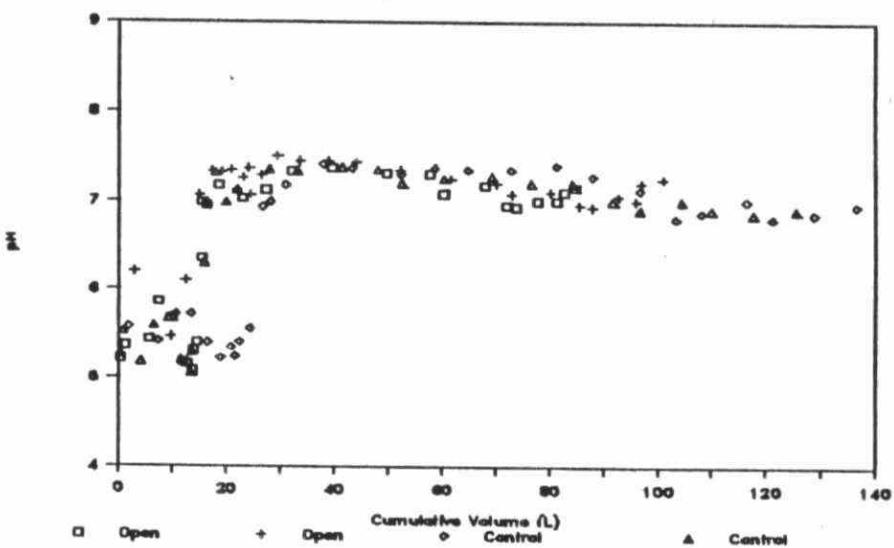


Fig.10a,10b: EFFECT OF CO-DISPOSAL ON LEACHATE pH

Fig11: Co-disposal 30% Industrial Waste

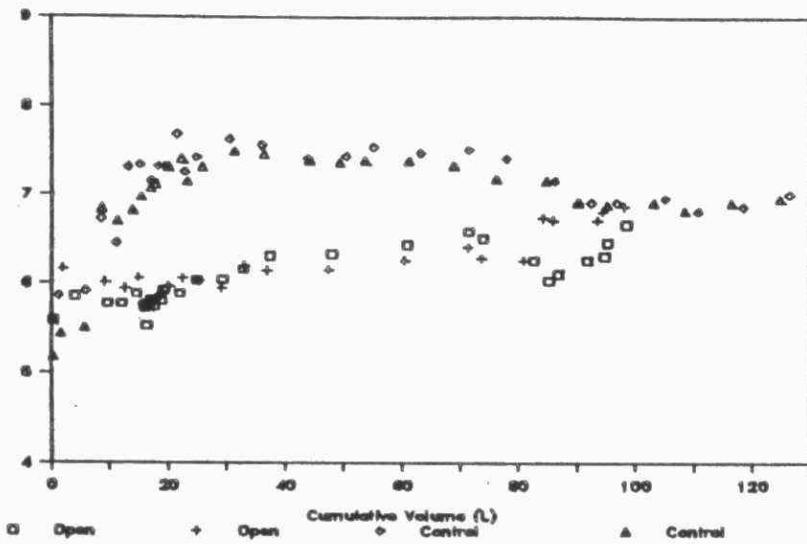


Fig.11: Leachate pH for Co-disposed 30% Industrial Waste.

Fig. 12: Relationship Between Eh and pH

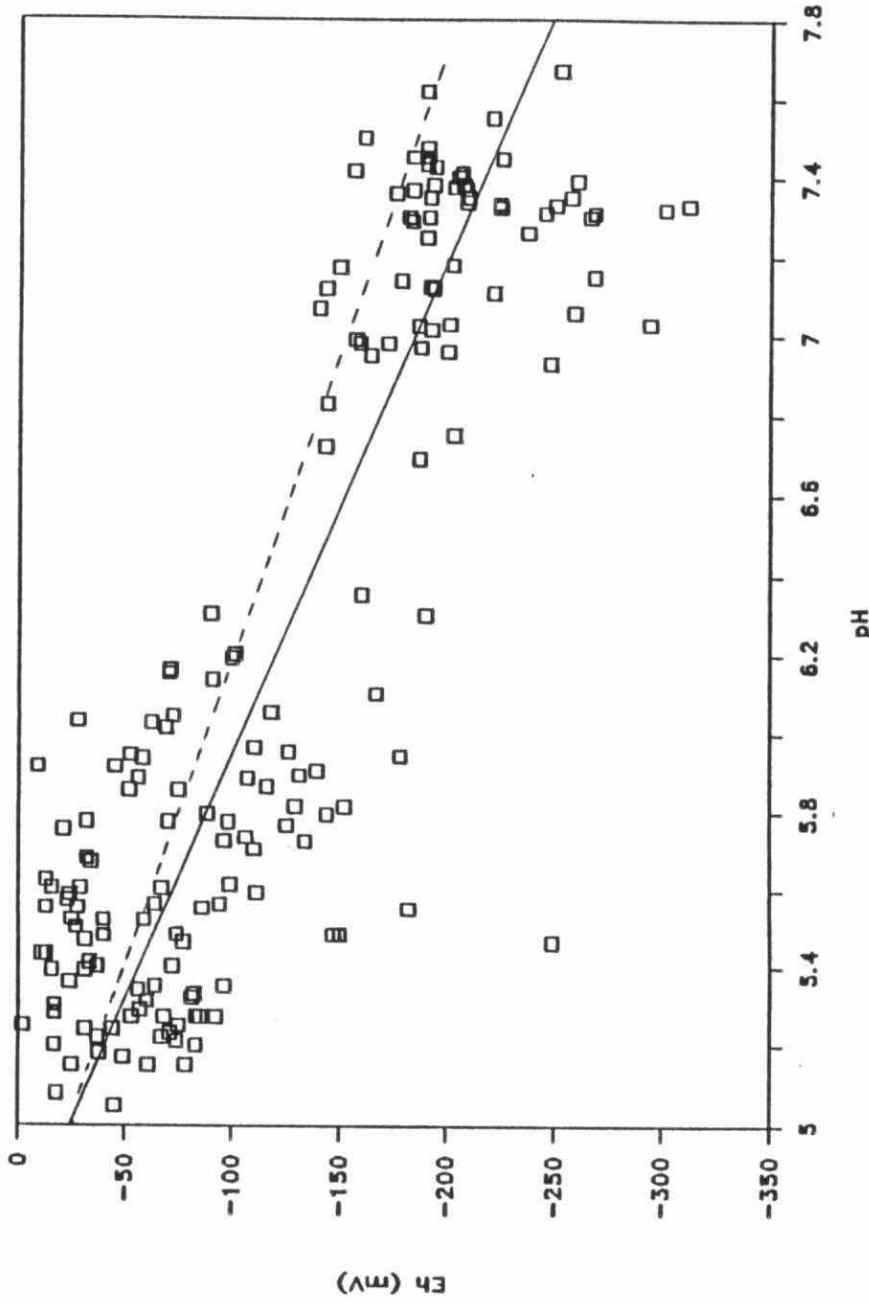


TABLE OF LEACHATE CHARACTERISTICS

	COLUMNS		
Leachate metal concentration	Very Low	Low	High
	13-16	4-8,11,12	1,2,3,9,10
pH value	(~12) 13-16	(7.4) 4-8,11,12	(5.5) 1,2,3,9,10
S concentration	(5ppm) 13-16	(100) 4-8,11,12	(300-600) 1,2,3,9,10
Leachate colour	(clear) 13-16	(brown*) 4-8,11,12	(tan*) 1,2,3,9,10

* air or light sensitive, darkens with time

From the grouping of the columns in the table it is clear that biological activity is a major factor in developing leachate composition. Since the presence of industrial waste suppresses metal contaminant concentrations, a modification of the microorganism population by the industrial waste is suggested. It is this aspect which bears careful investigation. The results of this work indicate that the presence of industrial waste exerts a favorable effect on the leachate quality. However the conversion of the test cells to more anaerobic conditions with time may reverse the favorable effect. Clearly, if the industrial waste does alter the biological activity in a municipal refuse environment then this could have a significant impact on methane generation. All of the implications of codisposal may not show up for a considerable period of time.

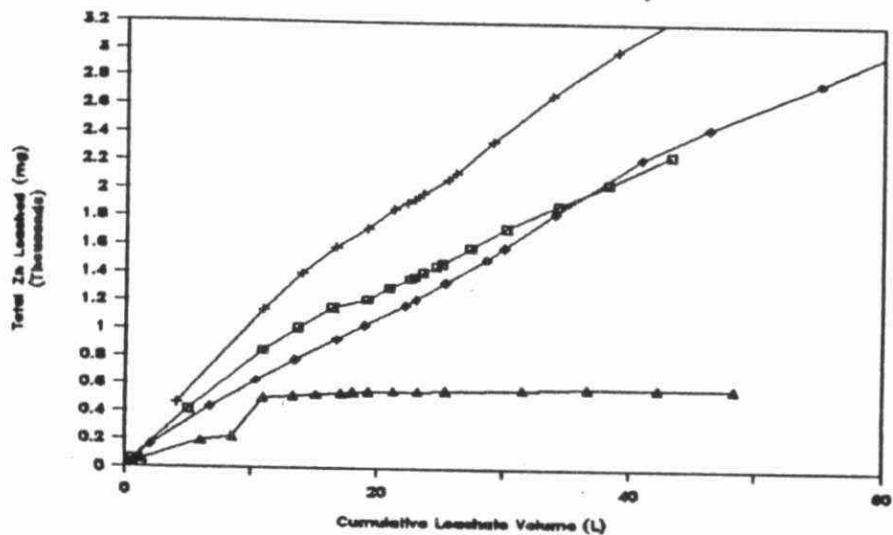
Summary

Experimental test cells designed for the investigation of factors affecting the stability of solids in a municipal refuse environment are operating and performing as required. The introduction of hazardous solid waste to the municipal refuse environment has not degraded the quality of the leachate generated in the early phase of landfill behaviour, and in fact has resulted in an improvement in the quality of the leachate. It is premature to recommend the use of codisposal since the test cells have not reached completely stabilized and thus may release more metal contaminants in the future. The mechanism of metal ion suppression is directly related to pH and Eh values, but these are in turn controlled by biological activity. Thus the role of the industrial waste in moderating the biological activity must be fully investigated. The research has demonstrated that short term leach tests and standardized EP or LEP leach tests do not provide adequate information on the mobilization of chemical species from solid wastes.

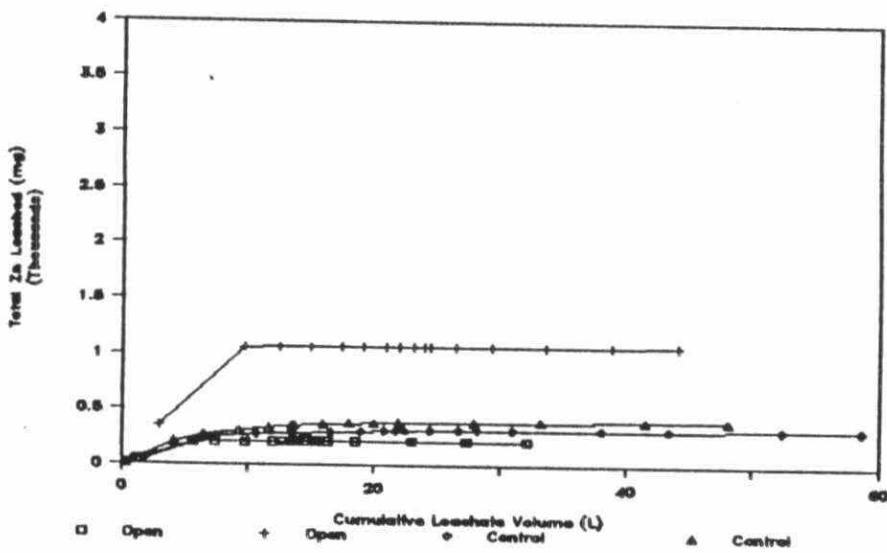
As more information is added to the data base, the significance of the various parameters becomes apparent, allowing better models to be developed for leachate generation. In addition to modelling leachate generation, analysis techniques should be developed to allow the identification of organically complexed metals. Preliminary species charge balances indicate the presence of organic ligands.

Appendix

Municipal Refuse Only

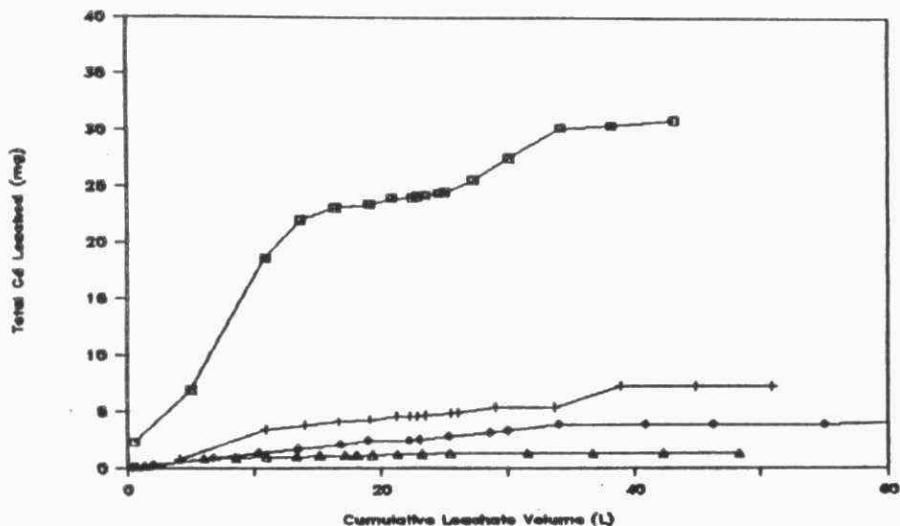


Co-disposal 8% Industrial Waste

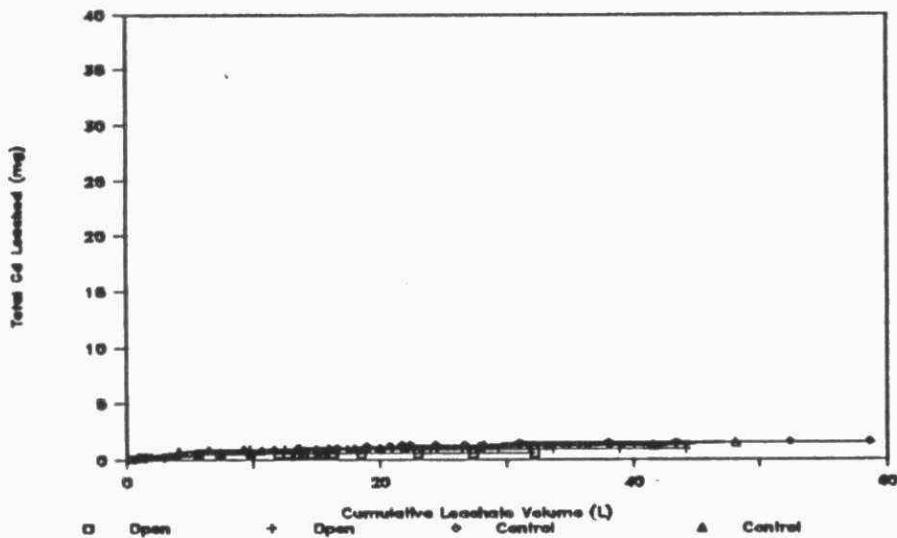


EFFECT CO-DISPOSAL ON TOTAL AMOUNT OF ZN LEACHED.

Municipal Refuse Only

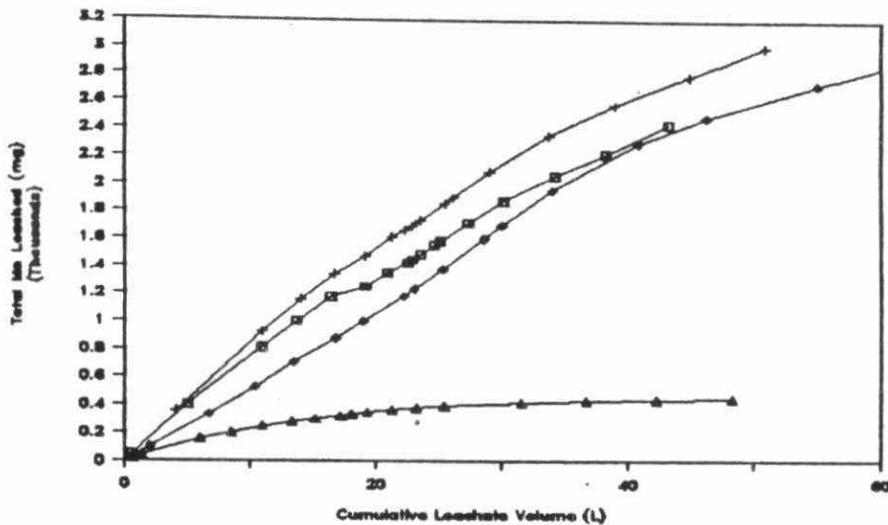


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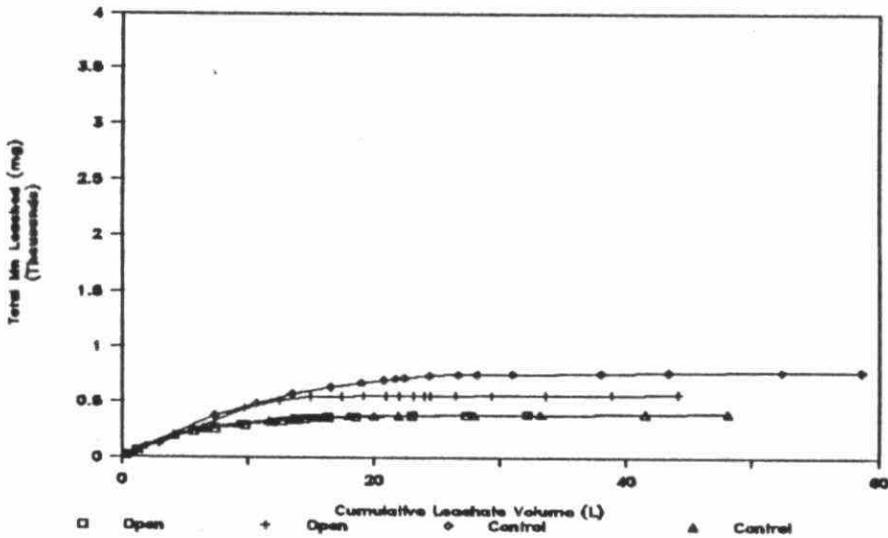


Effect Co-disposal on Total amount of Cd Leached.

Municipal Refuse Only

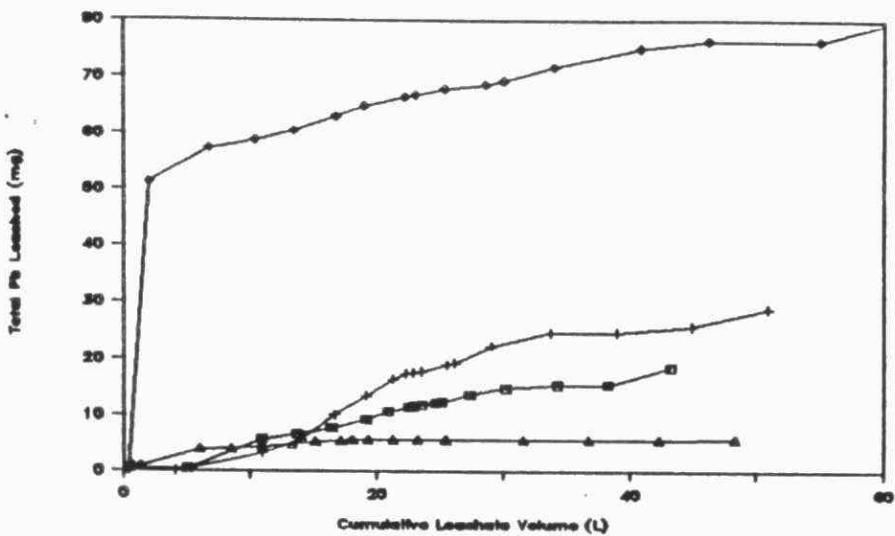


Co-disposal 8% Industrial Waste

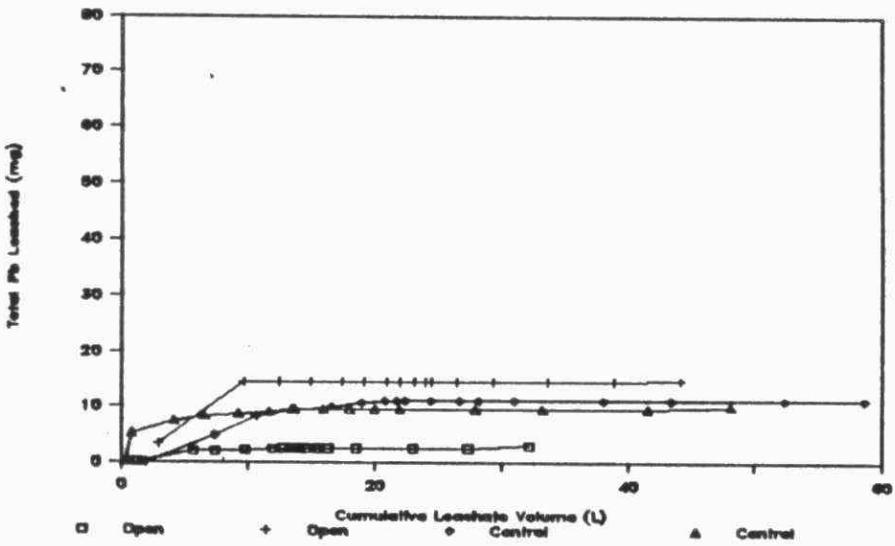


Effect Co-disposal on Total amount of Mn Leached.

Municipal Refuse Only

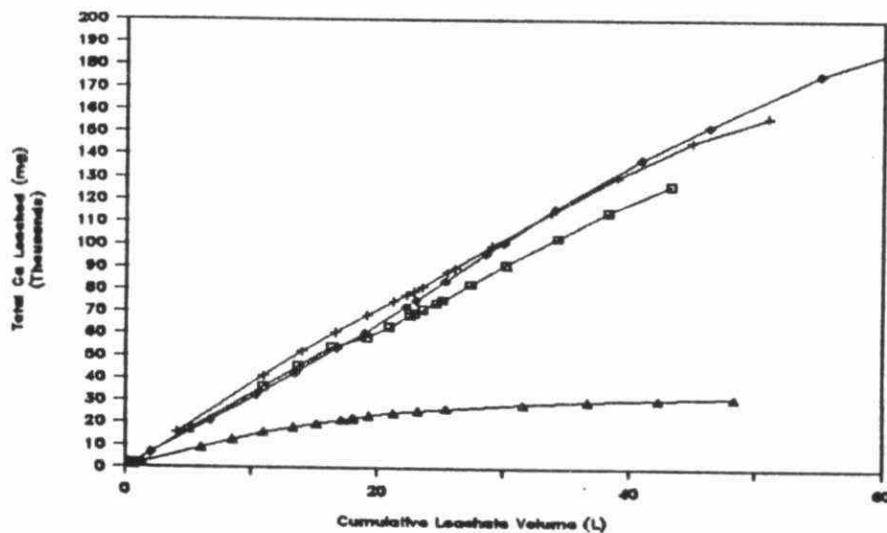


Co-disposal 8% Industrial Waste

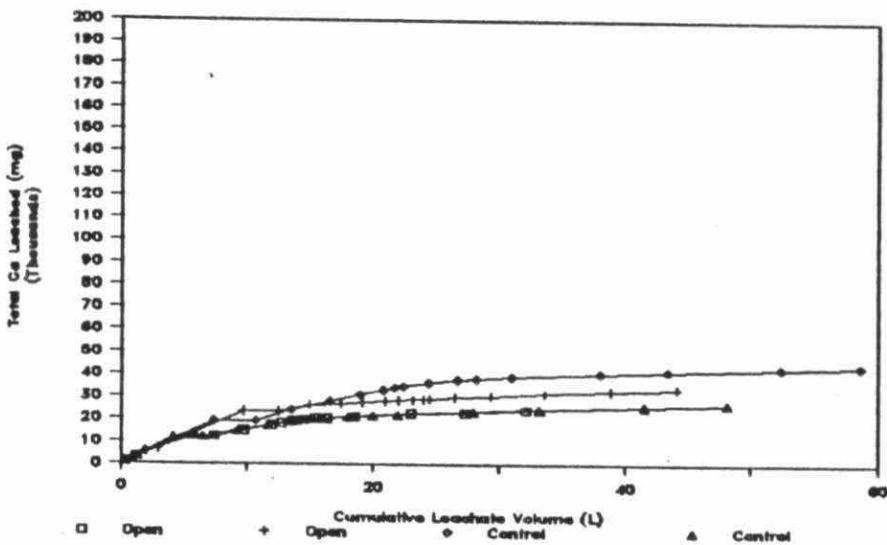


Effect Co-disposal on Total amount of Pb Leached.

Municipal Refuse Only

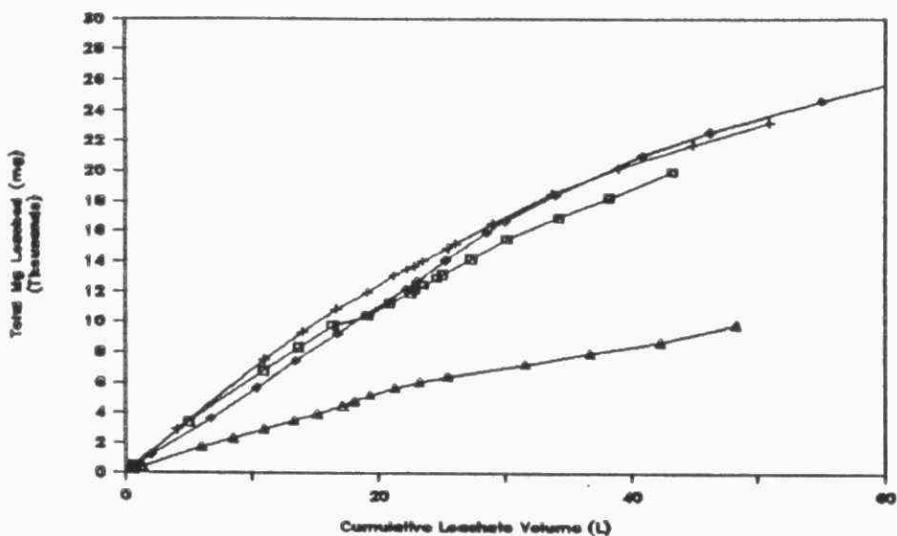


Co-disposal 8% Industrial Waste

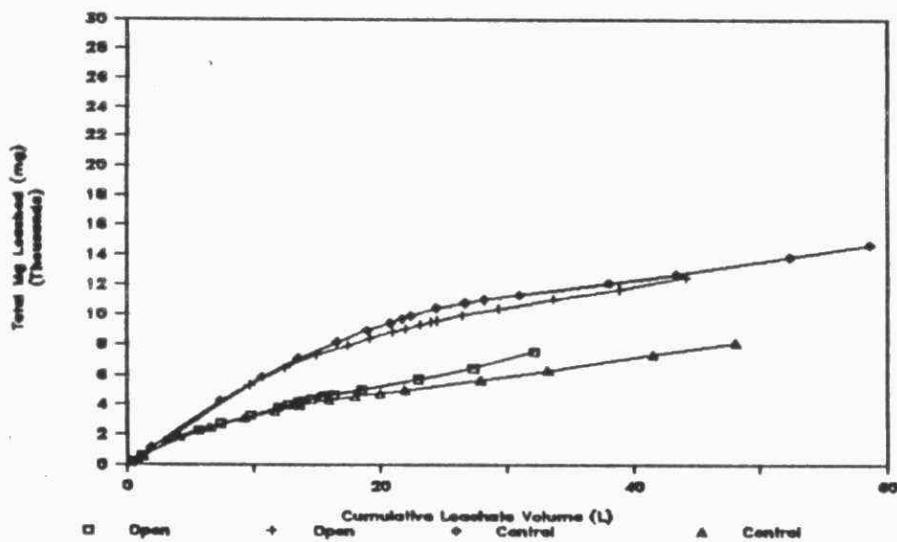


Effect Co-disposal on Total amount of Ca Leached.

Municipal Refuse Only

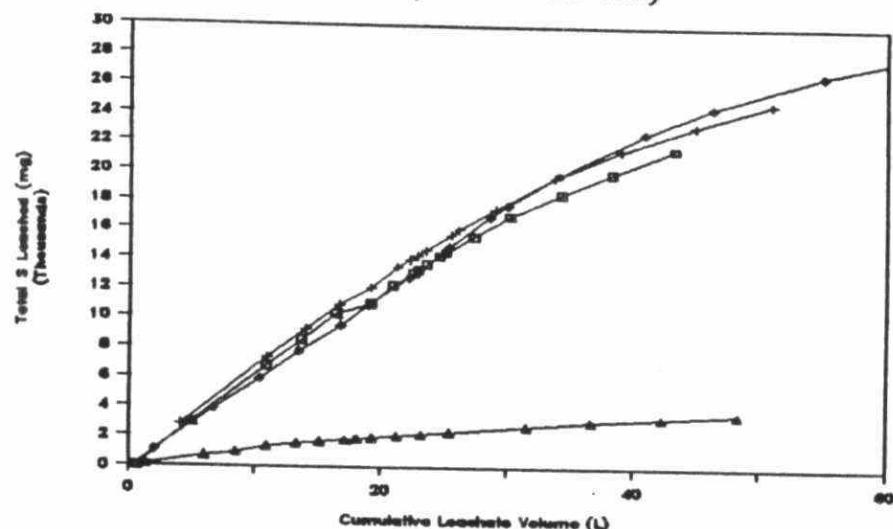


Co-disposal 8% Industrial Waste

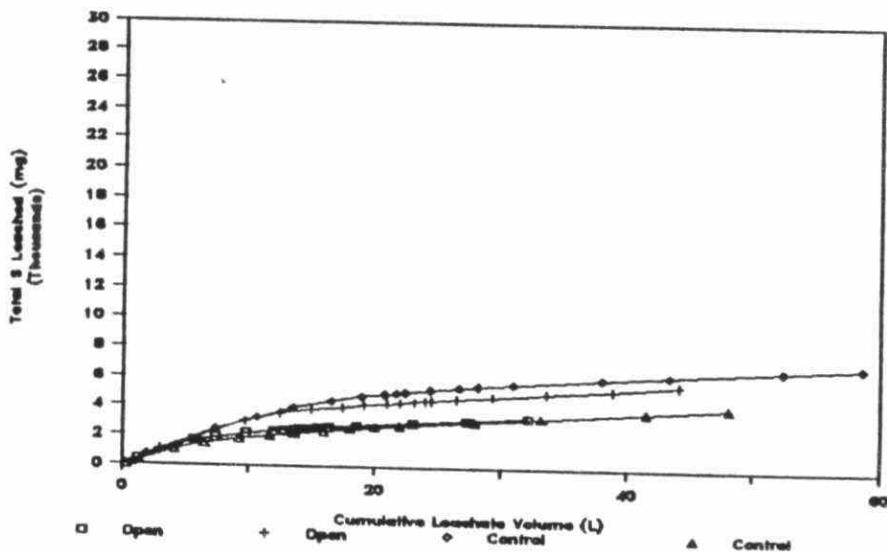


Effect Co-disposal on Total amount of Mg Leached.

Municipal Refuse Only

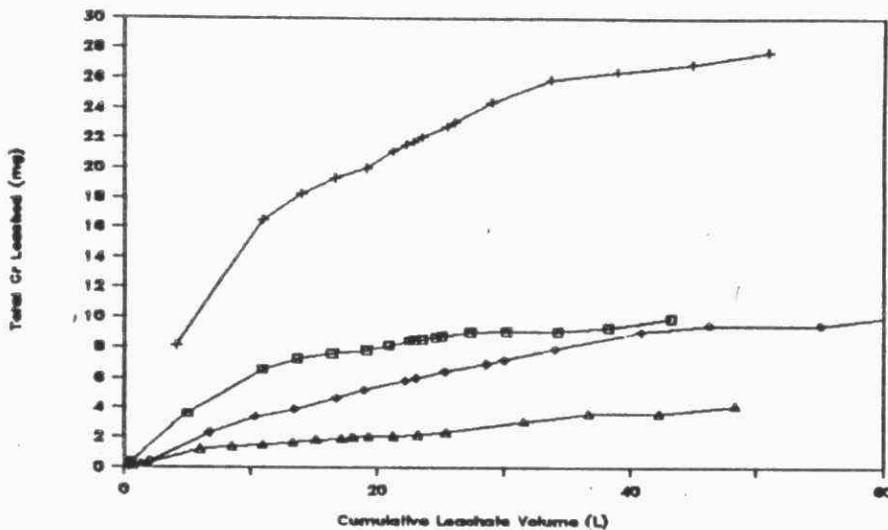


Co-disposal 8% Industrial Waste

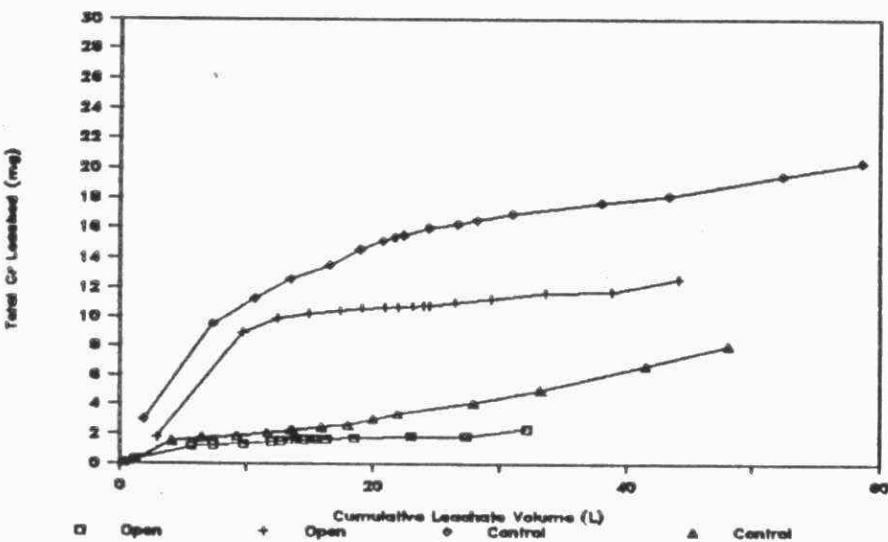


Effect Co-disposal on Total amount of S Leached.

Municipal Refuse Only



Co-disposal 8% Industrial Waste



Effect of Co-disposal on Total amount of Cr Leached.

Technical and Economic Assessment of Reverse Osmosis for the Treatment of Landfill Leachate

by

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ZENON Environmental Inc. Burlington, Ontario

Abstract

This engineering study involves the assessment of reverse osmosis (RO) technology as it may be applied to the treatment of landfill leachate waters. Preliminary testing involved evaluating pretreatment processes which may be appropriate for use before RO. Further testing will be conducted to examine the operation of a RO test system to determine its efficiency in removing contaminants and other performance characteristics such as flux rates and membrane life. The economics of RO as compared with other treatment technologies will be assessed in the final stages of this work. Work done up to date of printing indicates that pretreatment involving lime addition and microfiltration successfully reduces the TSS and iron level in the permeate which can then be processed by RO to remove dissolved organics and solids.

Introduction and Background

In recent years, the occurrence of a wide variety of organic and inorganic contaminants in ground and surface water has become recognized as a significant environmental concern by regulatory agencies. Many of the toxic and hazardous compounds commonly found in contaminated waters originate from landfill leachates, as a result of the soluble components of solid and liquid wastes being leached into the surface and groundwater.

Often these landfill leachates are comparable to complex industrial waste streams. In cases where drinking water supplies may be impacted or where there is surface breakout, remedial actions must be undertaken. At some landfill sites leachate which is collected is discharged to municipal sewers for treatment in conventional sewage treatment process. At other landfill sites where sewer lines are not available the leachate water may be hauled off site for treatment, may be recycled back to the landfill site or may be discharged to a surface water source. The expense of hauling leachate for treatment by conventional processes is expensive and new MISA regulations may limit the discharge of such complex wastes to municipal sewers. Recycling leachate within the landfill site itself can reduce the amount of liquid leaving the site for some time but effective and inexpensive methods of treating the material need to be developed.

Reverse osmosis has been successfully utilized as a waste treatment procedure for a wide variety of wastewaters. Some of these include wastewater from electroplating, petroleum, petrochemical, pulp and paper, food and beverage plants. Researchers have also investigated the possibility of using reverse osmosis for the treatment of landfill leachates.

Chian and DeWalle (1976) of the University of Illinois studied leachate characteristics and related these findings to the most effective treatment method to utilize. Data analysis of the ratios of parameters such as BOD/COD, and COD/TOC, revealed that the leachate from young fills containing mainly free volatile fatty acids can be degraded by biological means whereas old fills containing refractory organics were more effectively treated using physical chemical methods. They also concluded that of all the physical chemical methods evaluated reverse osmosis membrane treatment was the most effective in removal of COD from leachate water. They concluded further pretreatment of leachate prior to reverse osmosis processing would be necessary to prevent severe membrane fouling.

Slater of Manhattan College and Ahlert and Uchrin of Rutgers University (1983) investigated different treatment trains in conjunction with RO to treat landfill leachates. Pretreatment consisted of the removal of bulk oil using gravity separation, coagulation using lime, recarbonation, then pH adjustment with sulfuric acid. After each chemical addition the precipitate was allowed to settle before the supernatant was sent to the next treatment stage. The feed to the RO contained 16,400 mg/l TDS, 26,400 mg/l COD, and 8,480 mg/l TOC. The product water from the pretreatment train still contained the majority of the organic matter and the inorganic salts. RO treatment effectively removed 98% TDS, 68% COD, and 59% TOC. The permeate flux averaged $0.18\text{m}^3/\text{m}^2\text{d}$. Another pretreatment train investigated by these researchers (Slater et. al., 1986) involved lime coagulation, recarbonation, sedimentation, then biological treatment followed by filtration before RO. The RO unit was operated in concentration mode. The initial feed TDS and TOC were 13,180 mg/l and 110 mg/l respectively. Treatment by RO was found to be effective with an average TDS removal of over 99%. TOC rejection increased during the testing from 70.8% to 94.7%. The permeate flux averaged $0.29\text{ m}^3/\text{m}^2\text{d}$. Recovery was 63%.

In Canada, Environment Canada is the only public agency which has recently investigated RO for related applications. Over the last few years, a mobile self-contained RO unit has been used by researchers at EPS to demonstrate RO technology. Testing of this RO unit at a municipal landfill site containing hazardous wastes from government laboratories demonstrated that RO was an efficient method for concentrating dilute organic leachates (Whitaker et. al., 1985). High removals of organic contaminants such as 1,1-dichloroethane (85.3%), 1,2 dichloroethane (85.5%), diethyl ether (77.2%), 1,4-dioxin (86.6%) were achieved at a 10:1 permeate to concentrate ratio.

Work on this current project includes a technical and economic assessment of an optimized process for the treatment of landfill leachates. The scope of the testing involves pretreatment of a collected leachate sample using chemical addition and microfiltration (MF) to reduce the total suspended solids content and the concentration of potentially fouling chemicals such as iron, calcium and magnesium from feed to the reverse osmosis process. Reverse osmosis treatment will then remove the remaining dissolved organic and solids. The treated permeate could then be suitable for surface discharge. The concentrate produced from both membrane processes would require further treatment or off-site disposal. Figure 1 shows a potential process schematic. An outline of the work completed to date is presented.

Experimental Program

The experimental program for this work involves examining and optimizing pretreatment conditions followed by testing of reverse osmosis membranes and modules. A one drum (200 L) sample of leachate water was collected from a landfill site in Southern Ontario. A series of tests were conducted to determine whether caustic, lime, or lime with powdered activated carbon (PAC) followed by microfiltration would be the most effective pretreatment prior to reverse osmosis. The pH of 30 L of leachate was adjusted to 10 with either lime or caustic. In the third experiment the pH was adjusted to 10 by addition of lime and 20 g/L of PAC was added to the leachate water. The pH adjusted samples were then processed using 1/2" diameter tubular microfiltration membranes in a small membrane test unit. During each experiment flux rates were measured and permeate was collected for a 3-4 hour period of time. The permeate collected from each test was subjected to analysis for TSS, TDS, TOC, Alkalinity, Fe, Ca, Mg, and TOX.

The results of these experiments were used to identify the best pretreatment option for reverse osmosis. Work currently underway involves the treatment of a 2 drum (400 L) sample of leachate with the pH adjusted to 10 by lime followed by microfiltration. This pretreated water will be used for reverse osmosis membrane screening.

Initial reverse osmosis screening work will involve testing 4 different RO membranes in flat sheet test cells using pretreated leachate water. These experiments will give an indication of the flux rates and separations which can be obtained with these membranes. The results of these experiments will be used to select the best RO membrane for further experimental work.

The final test of the reverse osmosis process will involve the use of a spiral RO module and longer term (several days) testing using pretreated leachate sample. This final test will demonstrate the flux, flux stability and separation which can be achieved using reverse osmosis for the treatment of landfill leachate.

The final phase of work on this project will involve an assessment of the economics of the selected pretreatment and reverse osmosis processes relative to other processes which may be capable of achieving the same treatment objectives.

Pretreatment Testing Results

Significant differences were observed in permeate quality and flux rates with the different pretreatment methods used. Figure 2 shows the permeate flux rates over the course of the testing. The highest flux rate was obtained with lime pretreatment, where the initial flux rate was 300 US gallons per square foot per day (usgfd) but stabilized at 150 usgfd. A flux rate of 100 usgfd was obtained with the addition of lime and powdered activated carbon. The lowest flux rate of 19 usgfd was obtained with pretreatment using caustic.

Analytical results of the feed and permeate are presented in Table 1. Caustic pretreatment resulted in a 97.7% reduction in TSS and virtually 100% reduction in the concentration of iron, however there was an increase in the concentration of TDS and alkalinity. Lime pretreatment resulted in removal of 99.1 % of TSS, 16 % TDS, 11 % TOC, 46 % alkalinity, 10% calcium, 63% magnesium and complete removal of iron. A combined lime and powdered activated carbon pretreatment removed 99.5 % TSS, 28.3% TDS, 32 % TOC, 47 % alkalinity, 21 % calcium, 71 % magnesium and again 100% of the iron.

Lime pretreatment provided a significant reduction in TSS and iron, magnesium and calcium. A flux rate of 150 usgfd was obtained with this pretreatment. The combined lime and powdered activated carbon pretreatment results were promising, but this process would result in significant extra processing costs. Addition of lime met the objectives of the pretreatment with a minimal production of sludge and a lower cost than would be required if lime and powdered activated carbon were utilized. Based on these test results addition of lime followed by MF was chosen as the pretreatment method.

Conclusion

The results of the work conducted to date have demonstrated that lime precipitation followed by cross flow microfiltration can remove suspended solids and iron and reduce the levels of other components to produce a feed suitable for treatment by reverse osmosis. Experiments which will be conducted in the next few months will evaluate the suitability of RO in removing the remaining dissolved organics to produce a permeate suitable for discharge to the environment.

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Figure 1
Process Schematic

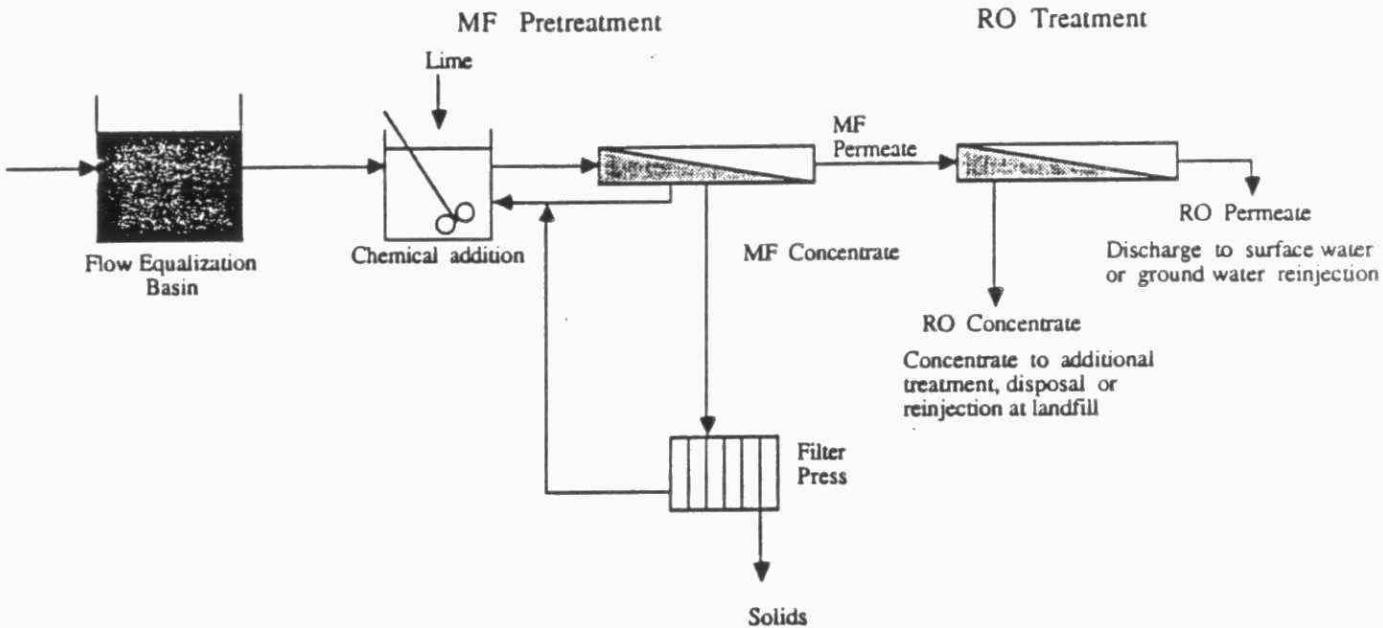


Figure 2
Microfiltration Permeate Flux Rates

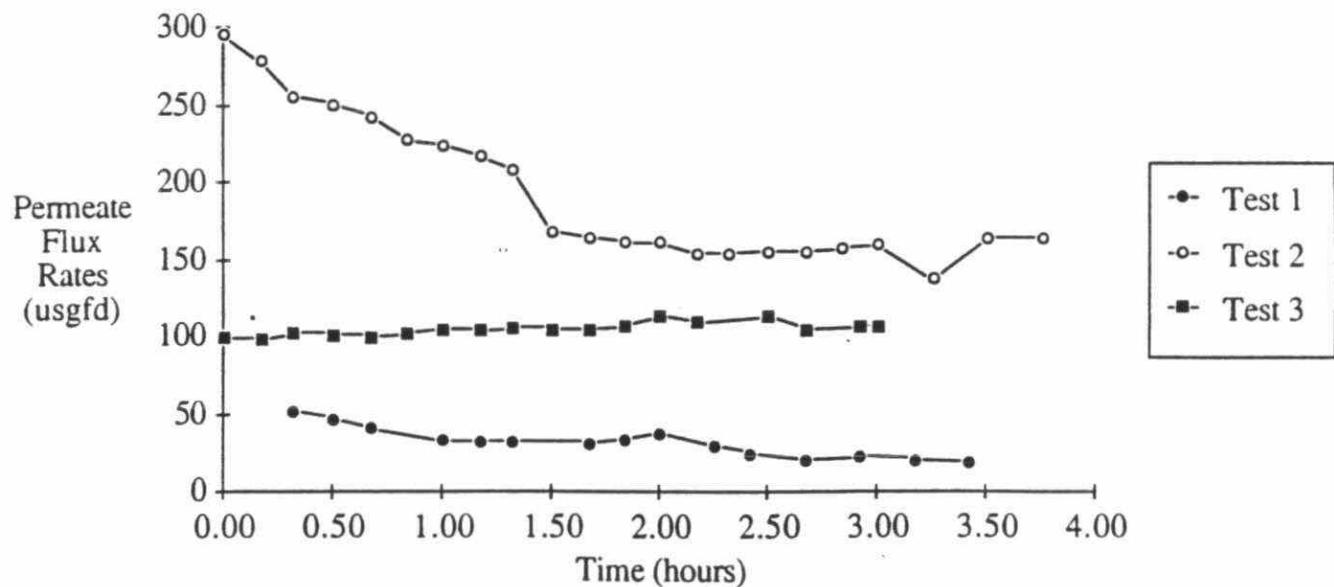


Table 1
Analytical Results of the Raw Feed and Microfiltration Permeate

Parameter (mg/L)*	Feed	Test 1	Permeate	
			Test 2	Test 3
TSS	290	6.5	2.7	1.5
TDS	6930	8530	5790	4970
TOC	1900	1710	1690	1290
Alkalinity	3740	4160	2000	1760
Iron	130	0.03	<0.01	<0.01
Calcium	570	5.7	510	450
Magnesium	380	200	140	110
TOX (ug/L)	228	108	31	4

* unless otherwise noted.

Enhanced Sanitary Landfill: A Demonstration Trial

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Introduction

Leachate generation at landfill sites continues to be a serious environmental problem. It is therefore necessary to address this with a suitable treatment scheme. The enhanced sanitary landfill (ESL) was developed at Ontario Research to provide leachate treatment and at the same time relatively fast land reclamation. This paper describes the concept of the enhanced sanitary landfill and the initial phase of a demonstration program which has begun at Peel Region's Britannia Road Landfill Site in Mississauga.

Nature of the Problem

The sanitary landfill has been and continues to be the principal means of municipal solid waste (MSW) disposal in Ontario. Through improved site operation such as contouring and compaction; health, environmental and aesthetic problems have been reduced considerably. Moreover, the application of final low permeability soil cover reduces the infiltration of moisture and hence the volume of leachate produced. Despite these advances, groundwater contamination by leachate, and toxic and combustible gas generation continue to be problems at many landfill facilities. The sanitary landfill is a land intensive process. With the trend towards fewer but larger landfills, MSW transportation costs have also increased. The uncontrolled generation of gas prevents the timely reclamation of the land for subsequent sale or reuse.

In the past, environmental authorities have relied on infiltration reduction and natural in-situ biological attenuation to deal with these difficulties. Methane recovery systems have been installed

at many landfills, providing a potentially profitable means of gas control. However, this system has several drawbacks notably, limited control over the rate of methane generation and very low methane recovery efficiency. As a result of these continuing difficulties, the Ontario Ministry of the Environment is seeking additional pollution control for sanitary landfills. Furthermore, with increasing public awareness of environmental matters and stricter regulations, municipalities are realizing that the sanitary landfill is no longer a cheap waste disposal option. In recognition of this need, a novel enhanced sanitary landfill has been developed.

The Enhanced Sanitary Landfill

Design Objectives

The proposed enhanced sanitary landfill process is designed with the following objectives:

- * To extend the life of the sanitary landfill.
- * To hasten land reclamation.
- * To enhance methane yield and quality.
- * To achieve a high degree of environmental control.

These objectives are achieved with a design incorporating as many conventional landfill management practices as is possible, in order to minimize additional capital and operating costs for the system.

The Concept

To meet the objectives outlined above, the enhanced sanitary landfill process must be designed so that the biodegradation rate of the MSW is maximized. It is believed that this can best be achieved by dividing the process into two stages, one occurring in the landfill site and the second in a separate vessel.

Stabilization of the waste is optimized by maximizing the leachate production in the landfill. The leachate is then removed to an anaerobic filter for methane generation. The treated leachate is recycled back into the landfill, to continue the process. It is estimated from published work that the organic fraction in the active landfill cell can be largely degraded in one to four years.

Saturation of the MSW is necessary to optimize the process. This is achieved initially through the infiltration of rainwater and the temporary redirection of surface run-off into the landfill. Once the saturation level of the waste is reached, then the recycled leachate will constitute the major flux into and out of the landfill.

The second essential feature of the enhanced sanitary landfill concept concerns the anaerobic digestion of solid waste which can be divided into three stages:

1. Hydrolysis and/or solubilization.
2. Production of volatile acids.
3. Conversion of volatile acids to methane (methanogenesis).

In the conventional landfill gas recovery system, all three steps take place in the landfill. However, the microbes which convert the organic fraction of the refuse to volatile acids are much more rapid-growing than are the microbes which convert volatile acids to methane. In the conventional sanitary landfill, this results in the accumulation of acids which causes the pH to drop and quickly inhibits the methane generation process. This new scheme which proposes the segregation of the methanogenesis step, results in accelerated and more complete conversion to volatile acids in the landfill site and improved yields and concentrations of methane in the methanogenesis digester.

The Process

The initial stage of enhanced sanitary landfill preparation is similar to that for a conventional sanitary landfill (see figure 1). The compacted waste is placed in cell formation on a low permeability soil, and daily and final soil covers are applied in accordance with good standard landfill practice. Perforated leachate collection pipes are placed on the cell floor prior to placement of waste. After completion of a cell and compaction of the final soil cover, perforated leachate recycle pipes are installed. Each cell is then brought to saturation as quickly as possible. Flow rates and composition of the recycled leachate are maintained to promote the solubilization of the waste and the subsequent production of volatile acids. It has been estimated that almost total degradation of the organic waste in the landfill should be complete within three years.

Leachate from the active landfill cells is then directed to a fixed bed of crushed limestone, where acids are neutralized and heavy metals precipitated as insoluble hydroxides and carbonates. This neutralization step protects the anaerobic filter from toxic loading of metals or excess acidity which would inhibit the performance of the methanogenic bacteria.

The leachate is then treated in the anaerobic filter which contains a high concentration of acclimated microbes capable of converting the soluble organics to methane and carbon dioxide. The microbial growth is established on a synthetic or crushed rock support medium. The gas generated should have a methane content of 75-80%. This is much higher than that conventionally recovered from sanitary landfill sites, where CO₂ from volatile acid production dilutes the recovered methane to a concentration of about 45-55%.

Comparison of SL with ESL

During the initial conception of the ESL, a computer model was developed to evaluate the process. The computer model determined the major engineering features and economics. It was also used to evaluate the sensitivity of the process to changes in compaction depth, solubilization rate, ambient temperature, leachate recycle rate and concentration of biomass in the anaerobic filter. The results of this engineering and economic evaluation were used to compare the ESL with the conventional landfill system in terms of leachate management, gas production, land reclamation and incremental costs. These comparisons are summarized below and presented in Table 1.

Unlike conventional landfill management which is concerned with preventing leachate formation, the ESL process seeks to maximize leachate generation by saturating the waste. The attenuation capacity of the underlying soil is improved by immediate removal in the leachate, of the solubilized refuse contaminants from the landfill. Heavy metals are concentrated in the limestone filter. The potential for fouling and clogging of the leachate collection system is reduced due to the constant immersion and exclusion of air.

Land used for landfilling wastes is not considered reusable for up to 50 years following landfill closure. It is estimated that in the enhanced landfill process, leachate and gas production in addition to land settlement will be substantially completed within three years of refuse placement. This means the ESL site should be ready for reuse many years ahead of the conventional landfill. Also, the municipality would be able to generate significant revenue from the sale and subsequent taxation of the reclaimed land.

Although capital and operating costs for a sanitary landfill are very site specific, and comparison of the two systems on an economic basis is difficult, preliminary estimates suggest that costs for the conventional landfill would exceed those for the ESL scheme. The methane yield from the ESL process is predicted to be over twice that of the conventional landfill and gas generation should be virtually complete within three years of operation. Furthermore, the methane concentrations reported for conventional gas recovery facilities vary from 42 to 55% (v/v), while the ESL should yield 74 to 85% (v/v) methane. Finally, with the enhanced sanitary landfill, methane production can be managed by controlling the leachate recycle rate, therefore permitting the adjustment of gas production to meet seasonal demands.

Pilot-Scale Demonstration

Phase I: Anaerobic Digestion of Leachate at Britannia Road Landfill Site

In order to further evaluate the concept of the enhanced sanitary landfill, a facility has been installed at Peel Region's Britannia Road Landfill Site, Mississauga. Phase one of this trial is a demonstration of the anaerobic digestion of leachate. The treatment facility is illustrated in Figure 2. The anaerobic digester is a 2m³ FRP/PE upflow fixed film reactor packed with Statiflow's modular media. The system will be operated over a one year period. Process variables such as gas production and concentration, temperature, hydraulic and organic loading, pH and alkalinity will be monitored and optimized through this phase. Start up of the facility is scheduled for September 1987. It is intended that extended operation of this unit will provide the necessary design information to scale up for phase II, in which the complete ESL concept will be demonstrated at Britannia Road.

Phase II: Integrated Enhanced Landfill System Study

Following successful completion of phase I, the enhanced sanitary landfill will be piloted with a demonstration unit. The integrated pilot project site is to be located at the Britannia Road Landfill. Although the results from the first phase will influence detailed design of the pilot facility the proposed system is as follows.

Two landfill cells (one enhanced cell for leachate recycle and one control cell for comparison) are to be constructed. Nominal dimensions of each cell will be 10m long by 10m wide. The cells will be separated by 2m minimum compacted clay fill. The cells will be constructed below existing ground level.

After initial excavation down to the specified bottom contours in the test cell area, a continuous synthetic membrane liner will be installed over the bottom and sides of the excavation. Protective cover material will be placed over the liner to prevent damage by heavy equipment. The collection piping system, surrounded with crushed limstone will be installed prior to commencement of landfilling in the cells. Surveying to record the initial ground contours of each cell will be undertaken. The refuse will be placed over the test area and the compacted clay separator installed.

A pumping station will be set up to provide leachate to the upflow anaerobic filter. The proposed system will include an in ground steel tank (3m diameter X 5m) with a fiberglass cover. The filter

media will occupy a volume of about 25 m³. Gases produced will be contained beneath the fiberglass cover. The production of gas will be metered and recorded prior to discharge to the waste gas flare stack.

A strict monitoring program will be conducted throughout the expected three year operation period. Piezometers will be installed to monitor the leachate surface profile. Core samples will be taken at selected locations for stratigraphical appraisal, and to allow installation of thermocouples and water level meters. Frequent inspection will be undertaken to ascertain flooding and circulation trends. Leachate and gas sampling and analysis will be conducted on a regular basis. Also, base level surveys of the cells to assess changes in surface elevation will be conducted. Soil-refuse core samples will be extracted periodically from each cell for physical and chemical analysis to determine the overall status and extent of waste degradation.

When leachate quality and gas production and quality are indicative of landfill stabilization, the recycling operation will be terminated. At this time, an intensive borehole/core sampling and analysis program will be initiated for each cell. The final sampling program will include a detailed survey of cell elevations, soil-refuse compaction, hydraulic conductivity, soil-refuse characterization, residual leachate quality and linear integrity. This comprehensive evaluation is essential so that any further leachate management/disposal requirements can be identified and so that the final status of the soil-refuse condition can be compared to the initial state when applied to the cells.

Acknowledgements

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TABLE 1 - Summary of Comparison Between Conventional
and Enhanced Landfill Processes

Landfill Design	
Conventional	Enhanced
* Minimize moisture intake	* Maximize moisture intake
* Air intrusion cause clogging and fouling	* No air intrusion-minimizes fouling
* Biological attenuation of leachate inhibited by metals and acidity	* Heavy metals precipitated-anaerobic filter at optimum conditions
* Gas production uncontrolled	* Gas production controlled
* Reusable after 50 years	* Reusable after 5 years
* Capital cost exceeds that of ESL	* Sale and taxation generate extra revenue
* Uneven gas production rate	* Gas production may be paced to demand
* Low methane recovery efficiency	* High methane recovery effeciency
* Methane content 42-55%	* Methane content 74-85%

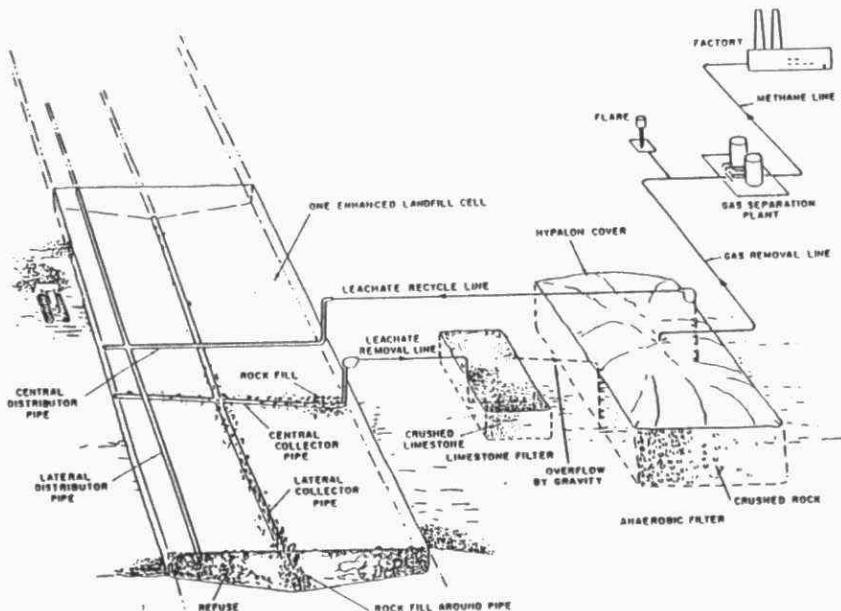


FIG. 1 ENHANCED LANDFILL SYSTEM

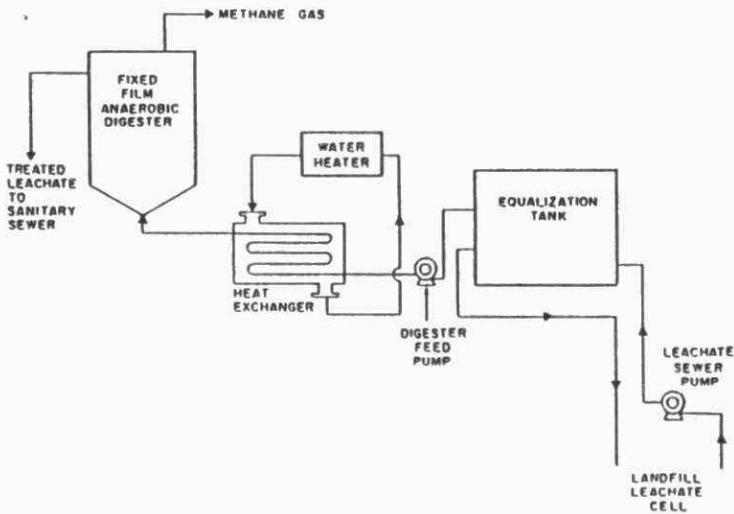


FIGURE 2. ENHANCED SANITARY LANDFILL : PHASE I DEMONSTRATION FACILITY

SEWAGE SLUDGE COMPOST AS TURF FERTILIZER

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Abstract

This study, supported by the Ministry of the Environment and the Ontario Ministry of Agriculture and Food is designed to evaluate the effectiveness of a sewage sludge compost as a fertilizer for fine and medium turf swards.

The sewage sludge compost and commercially available organic and inorganic turf fertilizers were applied at equal rates of nitrogen on irrigated and non-irrigated homelawn type turf and on creeping bentgrass turf maintained as a putting green.

Ease of application of the sewage sludge compost with a drop type fertilizer spreader was similar to other organic fertilizers on turf mowed at 4 cm, but tended to remain on the leaf blades of 5 mm mowed turf for an unacceptable period of time. There was no observable difference in winter injury, soil penetrometer readings, broadleaf weed invasion or proneness to disease between the sewage sludge compost and other commercially available organic or inorganic nitrogen fertilizers.

The paper will examine the effect of sewage sludge compost on the botanical composition of the creeping bentgrass-annual bluegrass sward, thatching tendency of the irrigated Kentucky bluegrass sward and the drought avoidance characteristics of the non-irrigated Kentucky bluegrass turf.

Introduction

Sewage sludge composts produced by the Beltsville aerated pile method has been used successfully in the growing media of various non-edible horticultural crops: bedding plants (Chaney, *et al.*, 1980), container-grown woody ornamentals (Sanderson, 1980) and nursery sod production (Murray, 1981). Eggens (1982) found that composted sewage sludge was as effective as sphagnum moss peat as an organic amendment for turf root zones receiving compaction stress. Murray and Juska (1977) suggested that organic fertilizers promoted thatch accumulation in Kentucky bluegrass turf to a greater extent than inorganic fertilizers.

Annual bluegrass (*Poa annua L.*) is a major component to turfs on athletic fields, lawn bowling greens and golf courses in Ontario. While it is generally considered to be a major grass weed, cultural and chemical weed

control practices have been relatively ineffective in preventing its invasion into and dominance of high maintenance turf swards. Because of the extensiveness of annual bluegrass in these turf areas, turf managers have attempted to maintain it somewhat as a permanent turf cover. The results from Waddington, et al., (1978) and Engle and Bussey (1979) suggests that annual bluegrass is less competitive with creeping bentgrass on putting greens when the nitrogen is from an inorganic source such as urea or a synthetic organic source such as Ureaformaldehyde than when the nitrogen source is an organic fertilizer such as Milorganite. While some researchers have attempted to relate phosphorus (Waddington, et al., 1978) and micronutrients (Morgan, 1982) to this response, the reasons for this response is not well understood.

The objective of this research is to determine the suitability of the Windsor composted sewage sludge as a general turf fertilizer and compare the response of annual bluegrass to the Windsor composted sludge and Milorganite.

Materials and Methods

The composted sewage sludge was material from the sewage treatment plant, Windsor, Ontario, which was composted according to the United States Department of Agriculture, aerated rapid composting procedure. It consisted of approximately 70% solids and 30% water. It was supplemented with sulfur coated urea to raise the nitrogen content to that of Milorganite so that the materials were applied at the same rate.

Screened Compost Analysis from the West Windsor Pollution Control Plants

Element	mg kg ⁻¹	Element	mg kg ⁻¹
NH ₃ -N	2,800	Chromium	390
NO ₃ -N	230	Copper	400
TKN	16,400	Iron	72,900
Phosphorus	19,400	Nickel	202
Potassium	1,000	Molybdenum	11
Arsenic	9	Mercury	2
Cadmium	8	Lead	309
Cobalt	4	Zinc	1,390

The remaining nitrogen sources are commercially available. Milorganite was 6-2-0, Canagro 12-6-6 and Sulfur coated urea was 31-0-0.

The first experiment (started October 1985) was conducted at the Horticultural Research Station, Cambridge, Ontario, on a 5-year-old mixed Kentucky bluegrass, annual bluegrass, red fescue, creeping bentgrass turf. The turf received medium management and irrigated as required to prevent drought stress. Nitrogen from Urea, Milorganite, and Windsor composted sludge (+urea) was applied 8 times from April to October to supply 0, 100, 200, 400 and 800 kg N ha⁻¹ over the growing season. The Windsor compost and Milorganite were applied at equal rates of product.

Experiment #2 commenced mid-June 1987, on a mature Kentucky bluegrass-red fescue turf mowed at 4 cm without regular irrigation. The plots received nitrogen from inorganic (SCU) and Organic (Milorganite, composted sewage sludge and Canagro) nitrogen sources applied at 100 kg N ha⁻¹ for a total of 300 kg N ha⁻¹ from mid-June to late August. The treatments were arranged in a randomized complete block design with 4 replications.

Experiment #3 commenced mid-June 1987, on a mature Kentucky bluegrass-creeping bentgrass turf mowed at 3 cm with regularly irrigated to prevent drought stress. The plots received relatively high rates of nitrogen from inorganic (Sulfur coated urea) and organic (Milorganite, composted sewage sludge and Canagro) nitrogen sources to stimulate thatch accumulation. The fertilizers were applied at the rate of 100 kg N ha⁻¹ per application for a total of 300 kg N during the period mid-June to late August 1987. The plots, 2 x 18 m were arranged in a randomized complete block with 2 replications.

Experiment #4 commenced mid-June 1987, in a mature creeping bentgrass-annual bluegrass turf mowed at 5 mm (clippings removed) and maintained as a putting green turf. The plots received nitrogen from inorganic (SCU) and organic (Milorganite, composted sewage sludge and Canagro) sources. The fertilizers were applied at the rate of 100 kg N ha⁻¹ per application for a total of 400 kg N ha⁻¹ during the period mid-June to mid-September. The wear treatments, light (3 passes) and heavy (6 passes), were applied with a drum roller with golf cleats. The main plots (nitrogen sources) were arranged in a randomized complete block design with 4 replications. The sub-plots (wear treatments) and overseeding treatments (slit-disc and multicore) were applied crosswise over all nitrogen treatments.

Results and Discussion

The first experiment started in 1985 has become seriously infested with rough bluegrass (*Poa trivialis*) and creeping bentgrass (*Agrostis palustris*) and will be terminated fall 1987. However during the three growing seasons the plots treated with composted sewage sludge maintained color as good as that obtained with Milorganite. Invasion of broadleaf weeds for all 4 nitrogen sources was similar. Penetrometer readings, a measure of the soil to resist compaction stress and an approximate indication of soil aggregation and aeration porosity of the soil, were similar for all N sources.

Table 1. Effect of N source on mixed turf maintained as a home lawn (started Fall 1985)

Treatment ^z	Color ^y 29 June	Broadleaf weeds (% of plot)	Pene- trometer (lb in ⁻²)
CaNU ₃	7.7ab	13.5a	48.4a
CSS	7.9a	10.0a	48.2a
Milorganite	7.1b	7.0a	47.7a
SCU	7.2ab	4.0a	48.0a

^zCSS = composted sewage sludge, SCU = sulfur coated urea.

^yVisual evaluation, scale 0 to 10, 10 dark green turf.

On non-irrigated Kentucky bluegrass turf, there was very little difference in turf color from all 4 nitrogen sources (Table 2). As would be expected the fertilized plots generally provided better color than the untreated control.

Table 2. Effect of N sources on non-irrigated Kentucky bluegrass turf.

Treatment	Color ^z			Appearance 18 July
	29 July	14 Aug	20 Aug	
Control	6.8b	6.3b	7.8b	7.0a
Canagro	7.8ab	7.8a	7.3b	6.3a
CSS	7.0ab	9.0a	8.8ab	8.5a
Milorganite	8.0a	7.8a	8.8ab	7.8a
SCU	7.3ab	8.8a	9.5a	8.0a

^zCSS = composted sewage sludge, SCU = sulfur coated urea.

^yVisual rating scale 0 to 10, 10 = darkest green;
appearance 10 = perfect turf.

The effect of N sources on turf color on the irrigated Kentucky bluegrass-creeping bentgrass turf (Table 3) was similar to that shown for the unirrigated Kentucky bluegrass turf (Table 2).

The pH of the developed thatch for the three organic N sources was similar while the pH for the SCU N source was significantly lower.

Table 3. Effect of N sources on irrigated Kentucky bluegrass turf maintained as a home lawn.

Treatment ^z	Color ^y		Thatch pH
	14 Aug	31 Aug	
Canagro	5.5b	8.0a	6.6a
CSS	8.0ab	8.5a	6.7a
Milorganite	8.5a	8.0a	6.5a
SCU	7.5ab	9.5a	5.7b

^zCSS = composted sewage sludge, SCU = sulfur coated urea

^yVisual evaluation 0 to 10, 10 = darkest green

On the creeping bentgrass turf, irrigated and mowed daily (clippings removed) the plots treated with the composted sewage sludge generally maintained turf color as good as the other nitrogen sources (Table 4). Compared to Milorganite the turf color on the composted sewage sludge plots was always as good as and on 3 evaluation dates, better than the Milorganite treated plots. The maintenance of color reflects the slow controlled release form the composted sewage sludge and the minimum amount of pick-up by the green mower after application.

Table 4. Effect of N sources on creeping bentgrass maintained as a putting green.

Treatment	Color ^y							Overall Mean
	15 June	21 July	29 July	14 Aug	24 Aug	31 Aug	4 Sept	
Control	3.3c	6.5c	6.5c	5.0d	5.0c	5.5c	6.0c	5.4
Canagro	9.0a	7.8b	8.0b	6.8b	8.3b	8.3b	7.8b	8.0
CSS	7.5b	8.3b	9.3a	9.0a	9.0ab	8.3b	7.8b	8.5
Milorganite	3.5c	8.3b	8.0b	7.8b	8.5b	7.8b	7.8b	7.4
SCU	7.3b	9.0a	9.0ab	8.5ab	10.0a	9.3a	9.8a	7.7

^zCSS = composted sewage sludge, SCU = sulfur coated urea.

^yVisual evaluation 0 to 10, 10 = ideal dark green turf.

Wear injury was generally more severe on the control, Canagro and SCU treated plots than on the composted sewage sludge and milorganite treated plots (Table 5). This may have been due in part to the hard granules of the Canagro and SCU being pushed into the leaf and crown tissue of the creeping bentgrass. The composted sewage sludge and Milorganite are a much softer material. It may also have been the result of the good controlled release

of the composted sewage sludge and Milorganite, providing a turf which was less succulent and less susceptible to injury.

Injury from both the slit-disc and the multicore overseeding was similar for all nitrogen sources (Table 5). The control which was not fertilized did not have the recuperative potential of the fertilized plots.

Table 5. Effect of N sources, wear and overseeding on creeping bentgrass turf maintained as a putting green.

Treatment ^z	Wear injury ^y			Overseeding	
	14 July	19 July	24 July	slit- disc	multi- core
Control	2.5c	1.5bc	1.0ab	3.0a	1.0a
Canagro	4.3a	3.0a	2.3ab	0.8b	0.0b
CSS	0.8d	0.5cd	0.0b	0.5b	0.0b
Milorganite	0.0c	0.3d	0.3b	0.5b	0.0b
SCU	3.3b	2.3ab	2.8a	0.3b	0.0b

^zCSS = Composted sewage sludge, SCU = sulfur coated urea.

^yVisual evaluation 0 to 5, 5 = most severe injury.

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DISPERSION OF THE STOUFFVILLE CONTAMINANT PLUME

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Introduction

A plume of contamination has developed in the Oak Ridges Aquifer under the Stouffville landfill site, located about 40 km northeast of Toronto, near the crest of the Oak Ridges Moraine (Figure 1). Waste disposal operations started around 1962 at the 0.74 km² site, and until 1970, this included both solid wastes and liquid wastes. Five natural depressions formed by glacial processes (kettle holes) were used as liquid waste disposal "lagoons" (Figure 2). In 1970, liquid disposal was banned, and only industrial and domestic solid wastes were received at the site. By 1974 all the "lagoons" were filled with solid wastes. The site closed in July 1985.

The site was first studied by consulting firms at the request of the Town of Stouffville. The Ontario Ministry of the Environment (MOE) reviewed the early reports and released a report on the hydrogeologic assessment of the site in 1982. A chemical and biological study of the groundwater at the site (MOE, 1982b) failed to identify mutagenic activity and concluded that there were no evidence of off-site contamination by the industrial organics present in the landfill. From 1982 to 1984, a hydrologic investigation was conducted by Conestoga Rovers and Associates (CRA) for the site owner, Waste Management Inc. (WMI), as a condition for completion of activities and site closure. Kaye (1986) studied the role of nearby

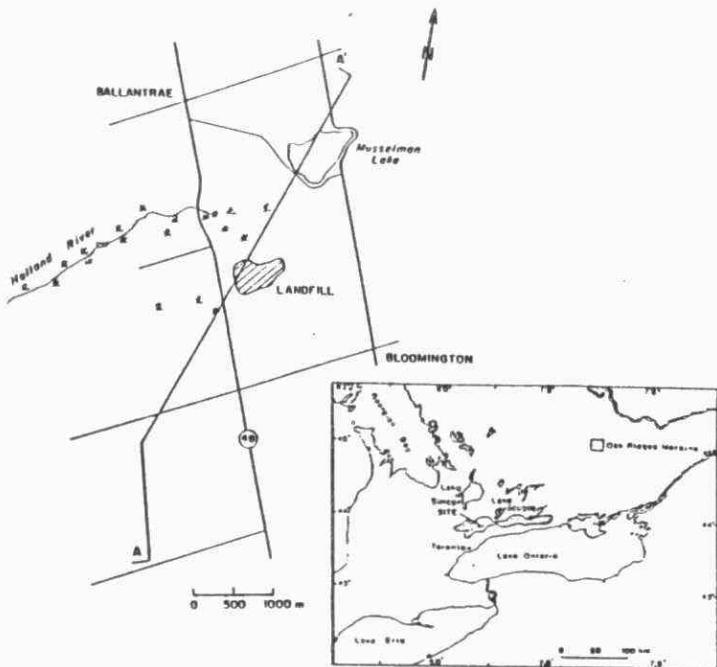


Fig. 1. Location map

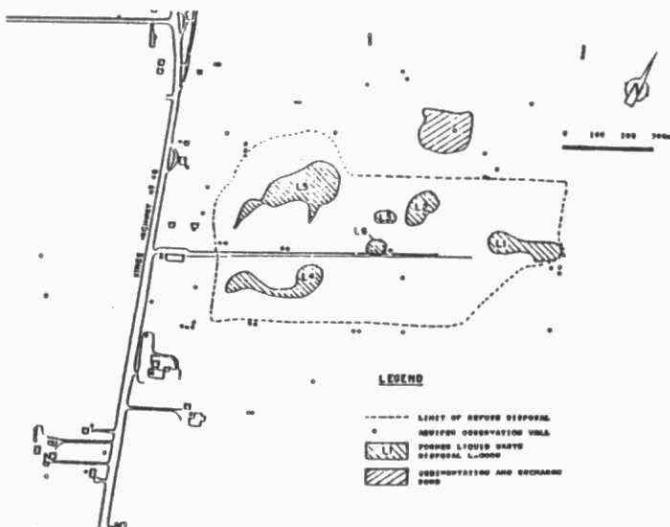


Fig. 2. Waste disposal site and aquifer wells
(modified from WMI, 1985)

Musselman Lake in the hydrogeology of the area. Duckworth (1979) described the stratigraphy of the Oak Ridges Moraine in the site area.

Since 1970, a total of 85 boreholes and observation wells have been installed on site. Twenty-one of them were completed in the main aquifer (Figure 2) and 17 penetrated the entire aquifer thickness. Geophysical logs were obtained from the 17 deep holes and used in conjunction with drillers logs to determine the hydrostratigraphy under the site.

Five hydrostratigraphic units were identified. The upper unit is a 0 to 20 m thick, clayey to sandy silt diamict, known as the Halton till. The hydraulic conductivity estimated from grain size analyses with the Hazen method varies from 1 E-2 to 3 E-7 cm/s. The internal stratigraphy of the Halton till in the site area is very complex and areally variable. Local perched water table systems are associated with the impermeable material, but at several places, the unit is unsaturated throughout suggesting high permeability.

The 34-44 m thick main aquifer is overlain by the Halton till except in the lowland to the north of the landfill where it is exposed (Figure 3). A thick unsaturated zone generally occurs between the Halton till and the water table in the main aquifer. The main aquifer is composed mostly of fine silty sands in the lower half, and subparallel beds of gravel and coarse sand surrounded by beds of laminated fine sands and silts in the upper half. Hydraulic conductivity estimations of aquifer sediments with the Hazen method range between 1 E-1 and 1 E-6 cm/s (WMI, 1985).

Three fine-grained units have been identified below the aquifer in test holes on the site. These units form an aquitard which is considered to represent the bottom of the flow system.

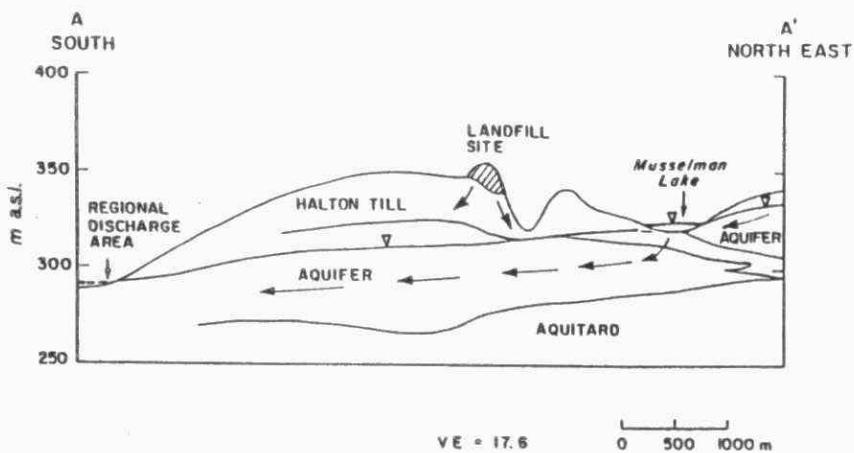


Fig. 3. Stratigraphy and flow system

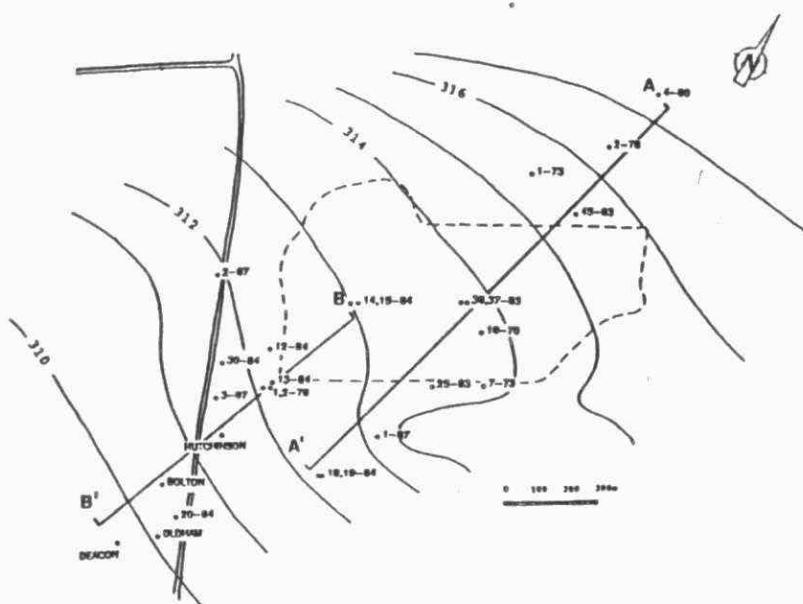


Fig. 4. Isopotential contours in 1986 (m a.s.l.)

Flow system

The water table configuration of the main aquifer indicates a southwest direction of flow with horizontal gradient as low as 0.004 (Figure 4).

The groundwater flow system under the site area is shown in cross-section on Figure 3. Musselman Lake receives discharge from a distinct water table aquifer to the north and at the same time is a source of recharge for the main aquifer under the site (Kaye, 1986). Additional recharge to the main aquifer occurs through the outwash material between the lake and the site. The bog area north of the site recharges the main aquifer and provides discharge to the East Branch of the Holland River during prolonged wet periods (WMI, 1985). Groundwater discharge also occurs in an east-west line of flowing wells and springs, 2 km south of the site.

Flow in perched water table systems of the Halton till is generally downward to the main aquifer with a limited horizontal component (Figure 3). Historically, the kettles have acted as surface water collection points draining most of the site (MOE, 1982a). Shallow aquifer wells of the sedimentation and recharge pond area indicate higher water levels in humid periods, but deeper aquifer wells are not affected as much by seasonal recharge. The influence of seasonal recharge is limited to the spring and fall periods.

Groundwater quality monitoring

The source of contamination in the aquifer, the lagoons and the refuse, are wastes and waste products located in the Halton till. Migration of the contamination is mainly downward through the till and the unsaturated zone toward the water table. Instead of trying to characterize in detail migration rates and pathways through those units, this study has focussed on contaminant migration in the aquifer. The water table in the main aquifer is the upper boundary of the system

that we are considering in our model. The strength of the contamination at this water table is the input function, and it can be monitored by water table wells. However, the relation between the different sources in the Halton till and early plume development must be considered to understand the present distribution of contaminants in the aquifer.

Early monitoring.

Quarterly monitoring of groundwater quality at the site started in 1970 in a limited number of on-site wells and private off-site wells and has produced an extensive record of chloride, conductivity, hardness, sulphate and phenol levels. The records show chloride concentrations to be less erratic with time than other parameters and chloride is therefore chosen for the assessment of early plume development. On-site wells of the center and southwest parts generally show a gradual rise in contaminant followed by a decrease. The chloride record of observation well (OW) 16-70 in the central part of the site shows earlier peak. Private, off-site wells to the southwest show a graduate rise in concentration that levelled off.

Infiltration of contaminants at the bottom of liquid waste disposal lagoons is a possible cause of the contaminant pulse recorded in downgradient wells. Lagoons 6 and 4 were the most permeable and received more wastes than the others (MOE, 1982a). The large amount of input at the water table might have caused mounding under the lagoons which modified the water table configuration as observed today. Contamination reached OW 16-70 and OW 7-73 at the same time, suggesting Lagoon 1 as the common source of the pulse in those wells and excludes Lagoon 6, located closer to OW 16-70. However, flow components from Lagoon 6 to OW 16-70 might have been important in the period of intensive liquid disposal in that lagoon. Reports of early investigations mention that the use of lagoons in the center area started before the use of the lagoon of the rear section (probably Lagoons 1

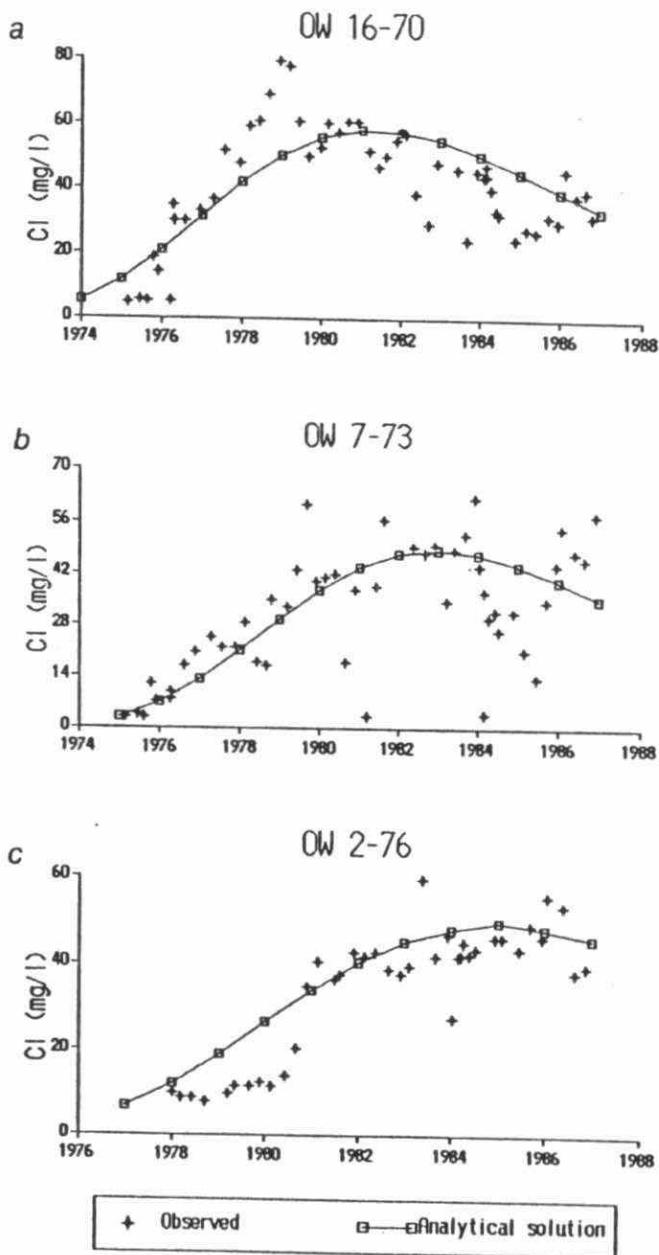


Fig. 5. 1-D transport simulations; (a) OW 16-70, (b) OW 7-73, (c) OW 2-76

and 2) (MOE, 1982a). Migration in highly permeable sediments of an early pulse from Lagoon 6 could explain the early part of the historical record at OW 16-70. Lagoon 4 in the southwest corner is a possible source for the pulse observed in the wells of that area.

A two-dimensional analytical solution of transport from a line source at the water table was applied to test the scenarios described. A source active from 1966-1970 was used, this interval corresponding to the most active period of liquid waste disposal (MOE, 1982a). Fast migration to the water table in permeable material near saturation under the lagoons was assumed. Arrival curves were obtained for OW 16-70 using a pulse Lagoon 1, a velocity of 20 m/y and a dispersivity of 18, for OW 7-73 using the same pulse, a velocity of 27 m/y and a dispersivity of 20 m, and for OW 2-76 using a pulse from Lagoon 4, a velocity of 16 m/y and a dispersivity of 15 m. Results are shown on Figure 5. The dispersivity values used are in the range found in the literature for the same type of aquifers and transport scale. Velocity values are variable across the site, but this was expected because of the variety of sediments forming the aquifer.

Recent monitoring.

The hydrologic investigation of the site by WMI from 1982 to 1984 brought about a considerable extension of the network of aquifer monitoring wells. The new wells became part of the quarterly monitoring program and in 1982 sodium, calcium, potassium, magnesium, alkalinity and dissolved organic carbon (DOC) were added to the list of parameters monitored. These data improved the delineation in plan view and cross-sections of the plume. In 1987, three more multilevel piezometers were installed to obtain more information at critical locations, providing another improvement in definition of the plume.

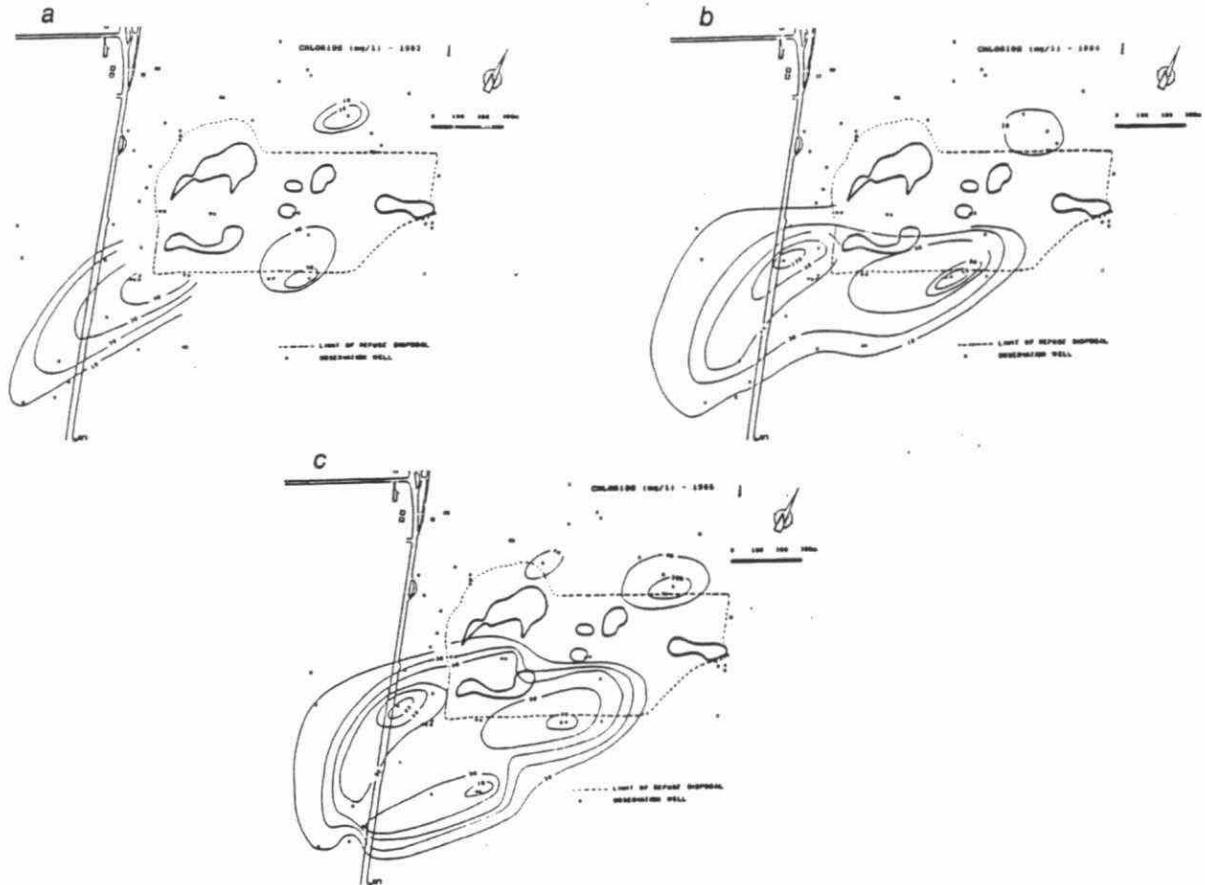


Fig. 6. Areal chloride isocontours (mg/l); (a) 1982, (b) 1984,
(c) 1986

Contours of chloride concentrations from 1982 to 1986-87 using the largest value measured at multilevel piezometers are presented on Figure 6. Yearly averages are used to reduce errors related to sampling and analytical procedures.

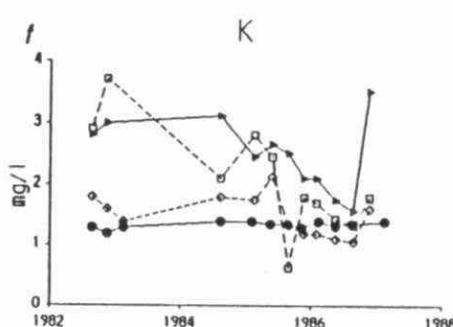
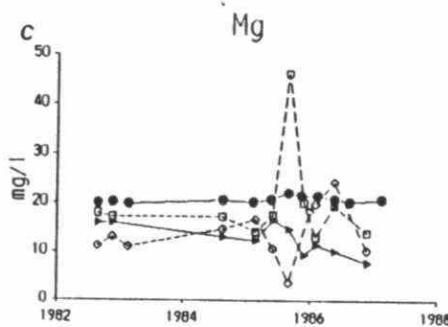
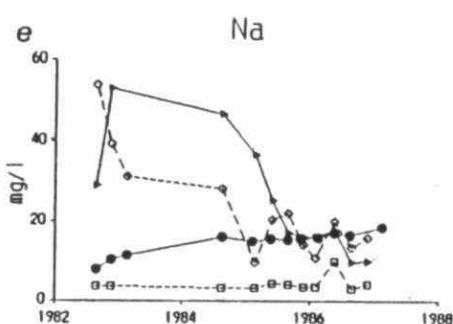
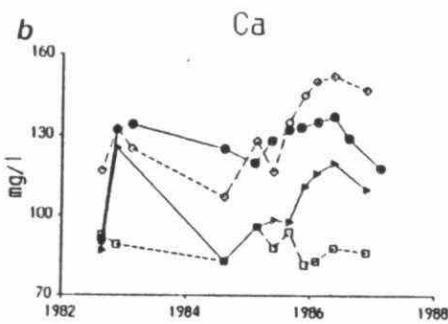
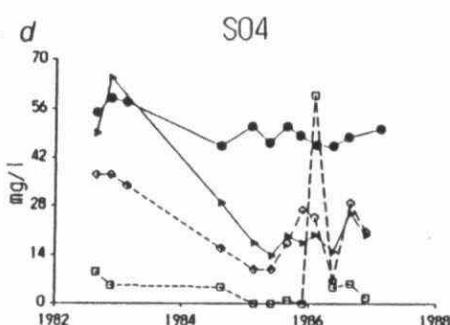
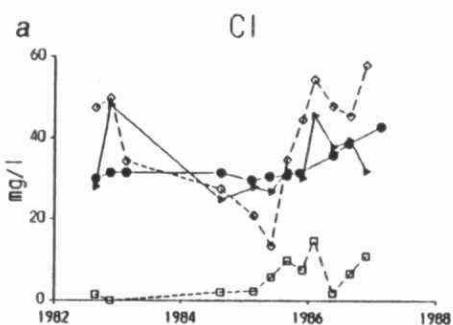
In 1982, the data show a plume in the southwest corner of the site with a core concentration of 45 mg/l and a good spatial distribution of the lower concentrations around it. A zone of elevated chloride is also identified in the center part and slightly elevated values are noted in the area of the recharge pond. Background levels are lower than 10 mg/l.

High chloride levels were found at two locations near the bottom of the aquifer in 1984. The peak concentrations of 126 mg/l in the southwest and 95 mg/l in the center can be contoured as the core of two small plumes contained in a broader envelope.

By 1986, the two peak values had decreased to 82 mg/l. An additional zone of high chloride concentration was found near the bottom of the aquifer, downgradient from the center plume, and three small plumes can be contoured in the envelope. Very high concentrations were measured in the recharge pond area and in general, upgradient chloride levels had increased.

Variations in contours from 1984 to 1986 indicate that the plume had migrated and dispersed, the peaks have decreased and the contours of lower concentration have spread. The plume configuration is the shape expected from the flow field, and it suggests that the source has ceased activity.

The increase in chloride levels upgradient is generalized and found at all depths. In some wells, the increase is considerable and concentrations reach levels usually observed in the plume. If downgradient and upgradient wells are affected by the same process, the variations in chloride levels downgradient are not simply related to plume evolution and such an assumption could distort the interpretation.



□---□ 2-78 ▶---▶ 16-70 ◆---◆ 17-73 ●---● Hutchinson

Fig. 7. Variation in major ions with time

Variations in levels of chloride, sodium, calcium and sulphate from 1982 to 1986 for representative wells are shown on Figure 7. The downgradient levels of sulphate and sodium decrease with time but sodium concentration is still increasing in the off-site well. Calcium concentration was increasing in the first part of the curve, but seems to now be decreasing. Chloride levels are still increasing in all wells. The chloride and calcium curves could indicate the expansion of a zone polluted by an active source or evidence of the approach of a migrating pulse of contaminated groundwater. In such a case, sodium and sulphate would be attenuated and the zone of elevated values of these parameters would be decreasing in extent.

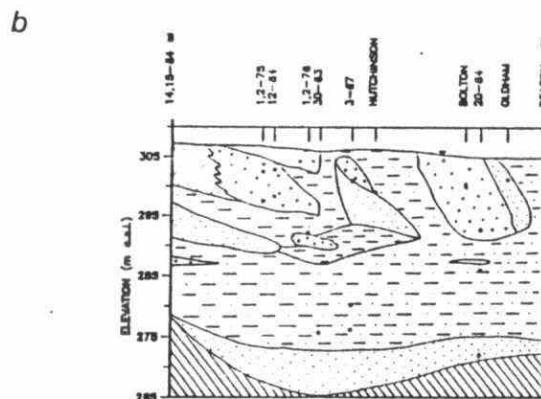
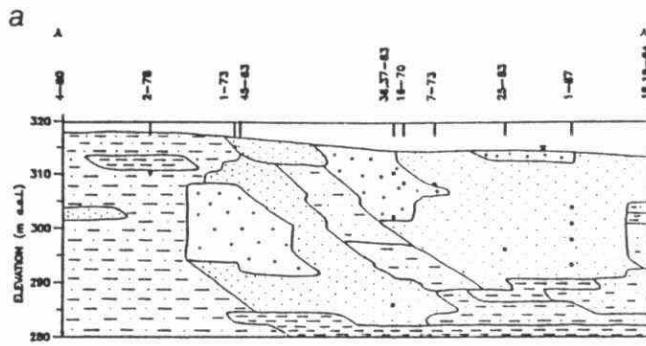
Plume delineation in cross-sections

In a stratified aquifer, the distribution of contaminants in cross-section has to be considered in detail. Different parameters were contoured in two aquifer cross-sections. The sections (Figure 4) are along the flow path and bisect the plumes defined in the broader envelope. Aquifer stratigraphy in the sections was drawn from borehole logs and Duckworth's (1979) description of the structures found in the fluvioglacial deposits forming the aquifer (Figure 8).

The parameters contoured exclude magnesium and potassium because their level is not elevated with respect to background.

Cross-section A-A'

Contours of chloride, electrical conductivity and calcium (Figure 9a,b,d) show a plume descending toward the bottom of the aquifer at the southwest end of the section. The peak level of calcium is located upgradient from those of chloride and conductivity, at OW 25-83. Sodium and sulphate contours show a plume of more or less horizontal orientation, with peak levels located at OW 25-83 also. The plume generally appears as a dispersed slug of contaminants with a rather regular



0 100 200 300m
VR = 15.17

LEGEND

GRAVEL	[Dotted pattern]	SILTY SAND	[Horizontal line pattern]
COARSE SAND	[Vertical line pattern]	CLAY	[Cross-hatch pattern]
MEDIUM SAND	[Solid line pattern]	TILL	[Diagonal line pattern]

Fig. 8. Aquifer stratigraphy in cross-sections; (a) in A-A', (b) in B-B'

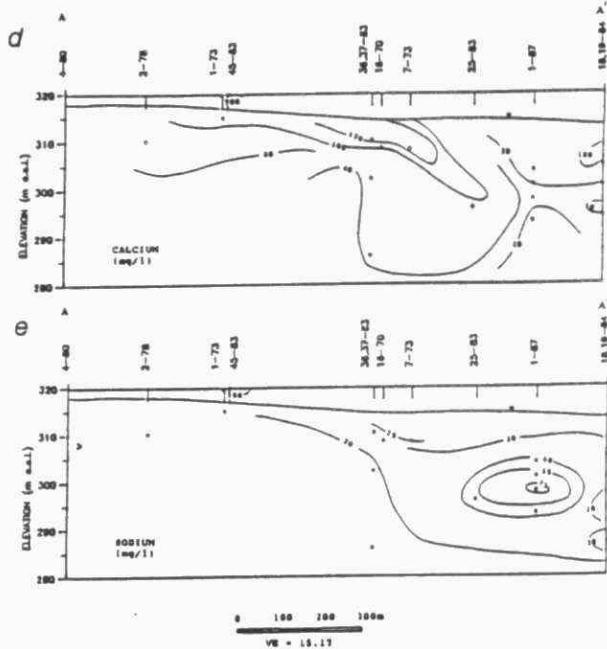
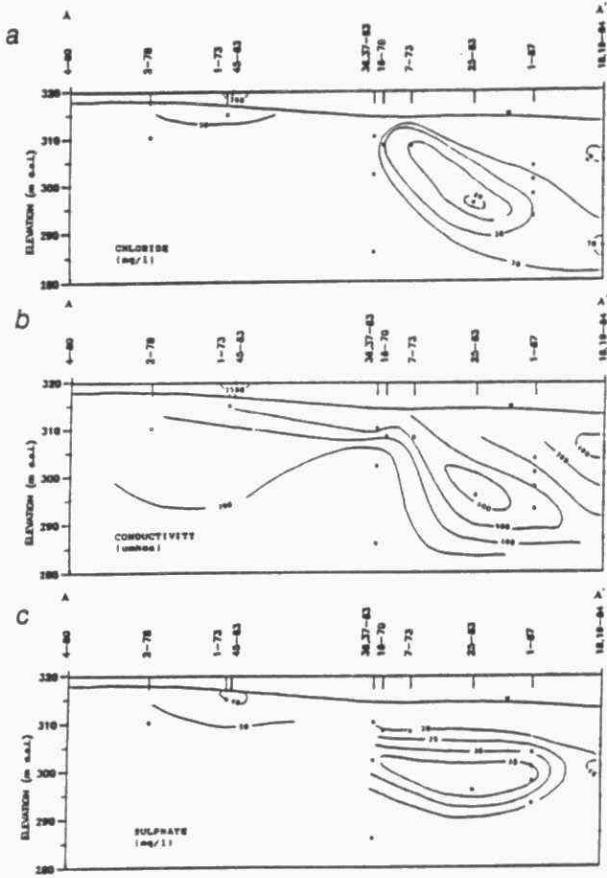


Fig. 9. Isocontours of constituents in groundwater (1986-87), cross-section A-A'

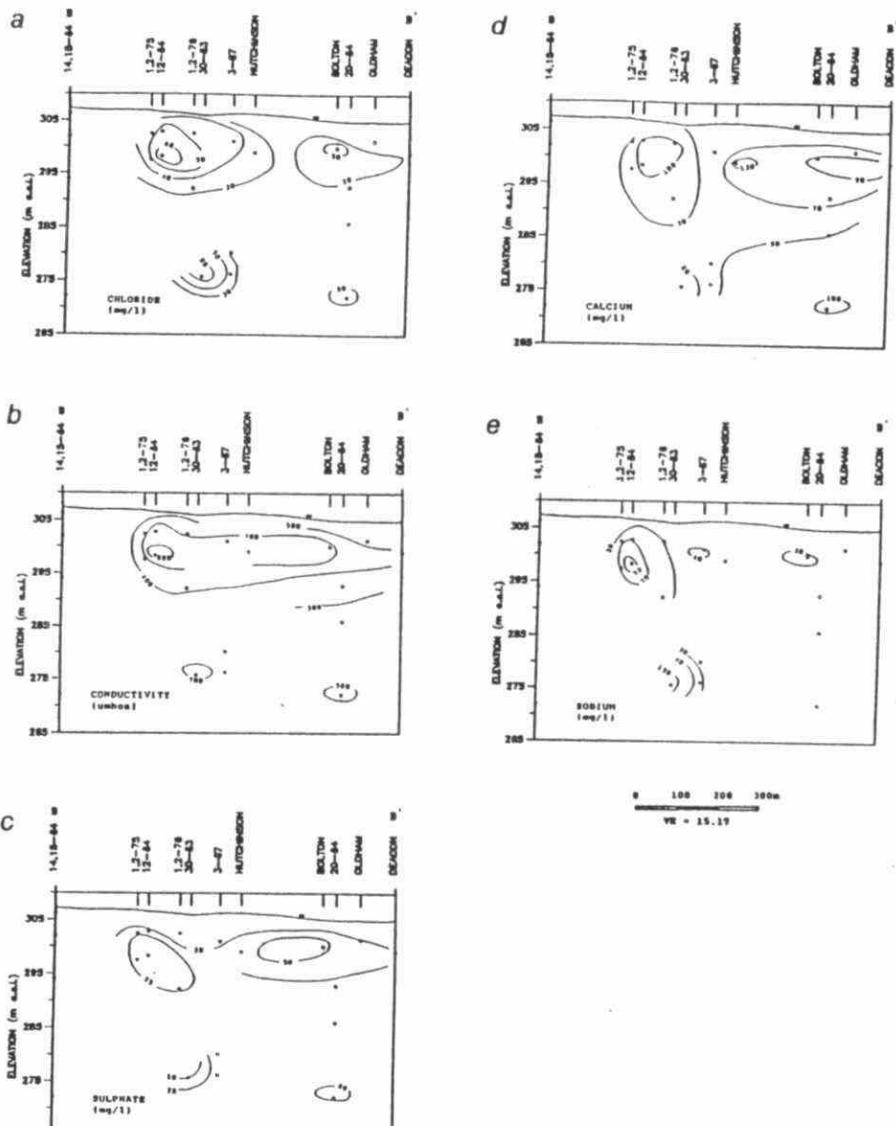


Fig. 10. Isocontours of constituents in groundwater (1986-87), cross-section B-B'

distribution of lower concentrations around the core. For all parameters except sulphate, levels much higher than these measured in the plume are observed at OW 45-83, upgradient.

Cross-section B-B'.

All parameters contoured in section B-B' show the same general shape and location of zones of elevated levels. Two zones are contoured in the upper half, the first one showing a vertical component of migration, the second one, located farther downgradient, has an horizontal orientation (Figure 10). For electrical conductivity and sulphate, these two zones could be contoured as one. Elevated concentrations are also observed near the bottom of the aquifer, but the limited number of data points precludes a good delineation. The concentration distribution shown by some parameters is similar to that of a dispersed front.

Tritium results in cross-sections.

Tritium is a radioactive isotope of hydrogen with a half-life of 12.43 years. The abundance of tritium is expressed in tritium units ($1 \text{ TU} = 1 \text{ }^3\text{H}/10^{18} \text{ hydrogen atoms}$). Before the start of nuclear testing in 1953, background levels were around 10 to 15 TU, which corresponds to levels below 2 TU today.

Water samples were collected in May 1987 for tritium analysis. The samples were analyzed at the Environmental Isotopes Laboratory of the University of Waterloo by direct liquid scintillation counting with a precision of +/- 8 or by gas counting after sample enrichment with a precision of +/- 5. Values measured in the aquifer range from 0.8 to 73.5 TU with a higher value of 122 TU observed in a shallow upgradient well. Samples with less than 15 TU determined by direct scintillation counting can be interpreted as having no significant tritium and this can also commonly be applied to samples having 15-20 TU (Edboka and al, 1983). In

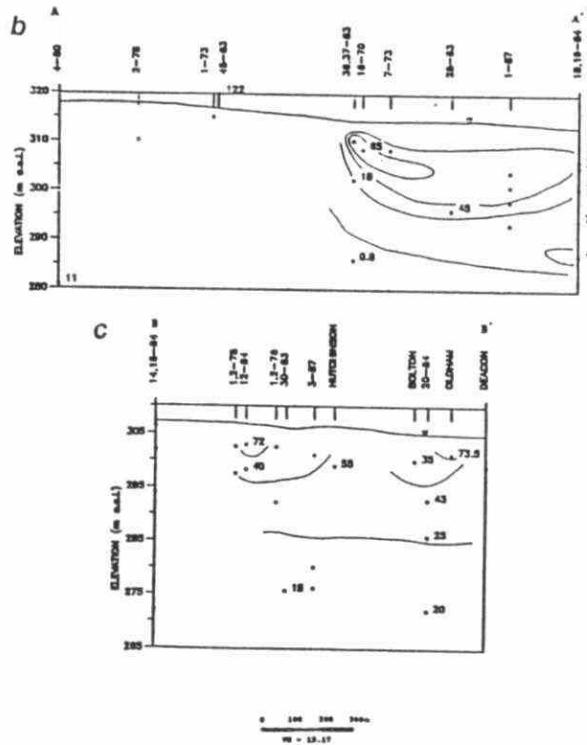
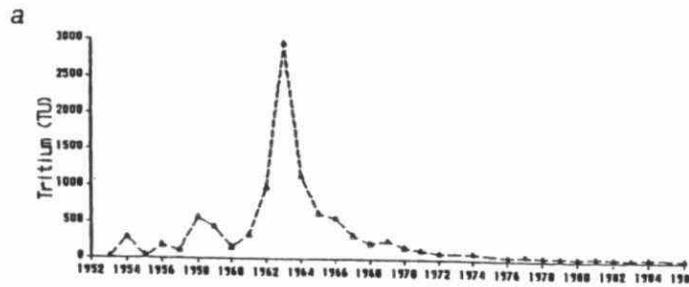


Fig. 11. Tritium concentrations (May 1987); (a) in A-A', (b) in B-B', (c) input function as a yearly weighted average

both cross-sections (Figure 11a,b) a zone of tritium with less than 20 TU is found in the lower part of the aquifer. These zones could represent water that entered the aquifer before 1953. A zone of low tritium is also found in the middle of the aquifer at the end of section A-A'.

The input function used in the interpretation of the results (Figure 11a) is a weighted average obtained from tritium concentrations in monthly precipitation at Ottawa and in southwestern Ontario. To account for values observed in the samples, the water must represent recharge during the period 1968-1970. Tritium transport in fluvioglacial aquifers is strongly influenced by dispersion (Edboka and al, 1983), which smoothes out the pulses of the input. The lower levels of concentration found downgradient and in the deeper zones might have been smoothed by the dispersion processes. The distribution of tritium in the cross-sections seems to indicate a plume similar to those obtained by contouring other parameters.

The 20 TU boundary could represent the limit between the active flow system and a zone of sluggish flow. In section B-B', the low values are found in the bottom half where sediments are generally less permeable. A clay layer is present between the upper zone and this lower zone.

The location of the highest value in section A-A' seems to indicate recharge occurred in Lagoon 6. In section B-B', the first zone of high tritium could correspond to recharge in Lagoon 4 while a second zone, downgradient, does not correspond to an obvious recharge zone at the surface. This could indicate fast horizontal transport with limited dispersion in the upper half of the aquifer.

The high value measured in the upgradient area could be the result of preferential infiltration of spring heavy rains, but it is difficult to evaluate when this occurred.

Flow simulations

Development of the contaminant plume was largely influenced by the local groundwater flow system. To obtain the flow patterns in the stratified aquifer, a numerical model was applied. The dual formulation of flow in terms of potentials and stream functions (Frind and Matanga, 1985) was used. The stream functions correspond to flow lines and allow a better visualization of the flow paths.

Cross-section A-A' is oriented parallel to the direction of flow and was chosen for simulations using this technique. The distribution of hydraulic conductivity in the section was obtained by assigning the Hazen hydraulic conductivity to the sediments forming each unit of the stratigraphic section.

The boundary conditions of the model were chosen according to field data. The northern end was represented by a flux, the southwestern end by a constant potential and the bottom was assumed impermeable. The water table was treated as a recharge boundary to avoid the possible spurious gradients caused by measurement errors, common in simulations using hydraulic heads at the water table boundary. Field data is not available for the liquid disposal years. In the simulation of these early conditions, it was assumed that the same boundary conditions could be used, except at the water table.

The recharge function for present recharge conditions is limited to recharge at the sedimentation and recharge pond, north of the site at a rate corresponding to the precipitation in the area (about 80 cm/y). Recharge conditions were different at the time of liquid wastes disposal. The sedimentation and recharge pond was not developed, but that area was probably draining part of the site. The recharge function of Figure 12b consists of recharge in the sedimentation and recharge pond area, recharge in Lagoons 1 and 2 located on each side of section A-A' at the same distance , and recharge in Lagoon 6 farther downgradient.

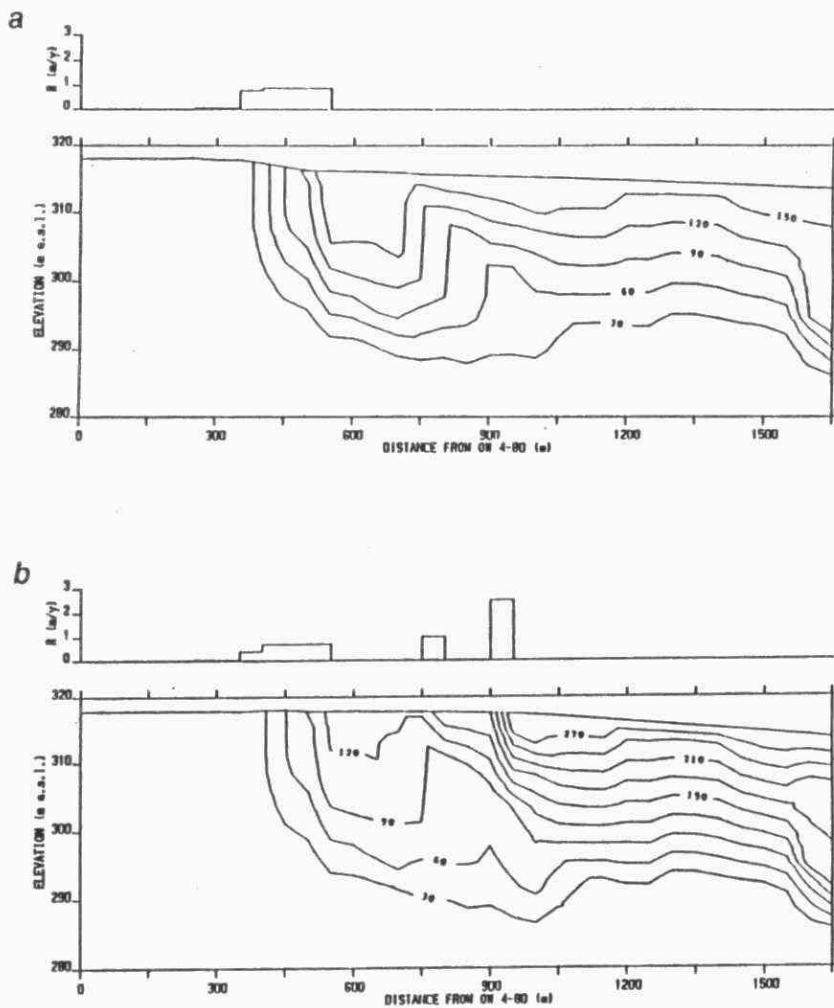


Fig. 12. Stream functions (square meters per year); (a) present conditions, (b) early conditions

Horizontal velocity calculated by the model for present conditions range from 0 to 81 m/y and average 11 m/y. For early site conditions, horizontal velocities range from 0 to 106 m/y and average 14 m/y for a recharge rate of 1 m/y in Lagoons 2 and 1, and 2.5 m/y in Lagoon 6. Recharge rates in the lagoons are unknown and the influence of their magnitude was tested. By doubling the recharge rates in the lagoons, a 17% increase of the maximum horizontal velocity was obtained, and the flow lines had a similar configuration. For all cases, the zone of maximum horizontal velocity was located in the lower half of the aquifer, at the downgradient end.

The flow fields obtained are largely influenced by the hydraulic conductivity distribution. The flow patterns obtained with the early recharge function are very similar to those obtained with the present recharge conditions with steeper flow lines under the lagoons. Downgradient from the lagoons, flow is mainly horizontal except at the end of the section in the lower part of the aquifer, where a significant downward component occurs.

Retardation of contaminants

Retardation of some inorganic pollutants in the aquifer was studied in the east section of the plume corresponding to the downgradient half of section A-A'. Magnesium and potassium were not studied because of their low levels. The variation along the flow path of sodium, calcium, sulphate and chloride is shown on Figure 13a. Variations in concentrations could be caused by source strength variations, hydrodynamic dispersion and chemical reactions or a combination of all three. No information is available on the source strength and this possible cause has not been considered. To distinguish between variations due to dispersion and chemical reactions, ratios of the conservative species chloride to the other species were calculated.

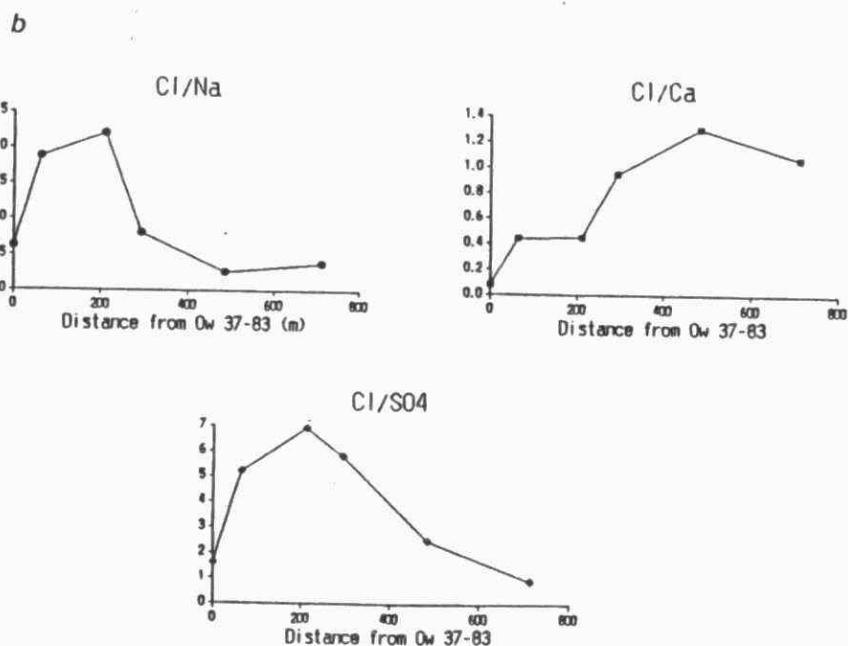
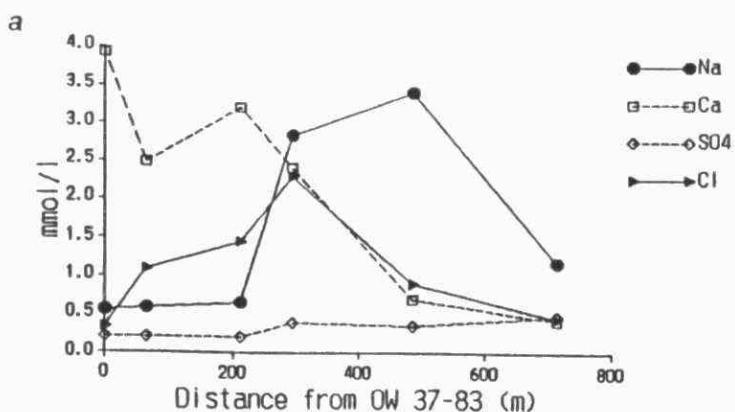


Fig. 13. Retardation in the aquifer (1986-87); (a) variation of major ions along the flow path, (b) chloride ratios

An increase in the ratio corresponds to attenuation by chemical processes, while a decrease indicates an addition of the species to the water. A constant Cl⁻/species ratio at the source was assumed.

The ratios of Cl⁻/Na⁺ and Cl⁻/SO₄²⁻ show the same trends; an initial increase to reach a maximum at OW 7-73, followed by a decrease. Na⁺ and SO₄²⁻ are added to the water until OW 7-73 where attenuation starts. OW 7-73 marks the extent of the Na⁺ and SO₄²⁻ contamination fronts.

The Cl⁻/Ca²⁺ ratio shows a constant increase along the flow path. Ca²⁺ is attenuated for the whole length of travel. Usually, Ca²⁺ is the main cation on exchange sites because it is the dominant cation in the groundwater and it is sorbed preferentially to other cations. Loading of other cations in the water by contamination often causes the elution of Ca²⁺ from the exchange sites (hardness halo) that is replaced by other cations. At this site, Ca²⁺ is the main cation in uncontaminated groundwater, but the only cation other than Ca²⁺ found at elevated levels is Na⁺. There is no evidence of Ca²⁺-Na⁺ exchange since Ca²⁺ levels are always decreasing. Precipitation/dissolution reactions might be responsible for variations in main ions levels not caused by dispersion.

Summary and conclusions

A variety of methods have been used to describe and explain the behaviour of the Stouffville contaminant plume. Fitting of a 2-D solution of transport from a source corresponding to liquid wastes disposed of in lagoons in 1966-1970 to observed chloride arrival curves resulted in average groundwater velocities ranging from 16 to 27 m/y, and longitudinal dispersivities between 15 and 20 m. Tritium concentrations in the aquifer indicated a zone of sluggish flow in the lower half of the aquifer except at the downgradient end of cross-section A-A', while water of

the upper half would represent recharge during 1968-1970. Areal chloride contours from 1982 to 1986 showed a spread of the plume and decrease of its peaks. The latest contours showed three plumes included in a broader envelope.

Contours of different parameters in cross-section A-A' showed two different plume orientation, a horizontal plume for Na^+ , SO_4^{2-} , and Ca^{2+} , and a plume descending toward the bottom of the aquifer at the downgradient end for Cl^- and conductivity. The ratios of Cl^- to Na^+ , SO_4^{2-} , and Ca^{2+} along the flow path indicated that their migration was retarded with respect to that of Cl^- .

Numerical simulations in cross-section A-A' showed the large influence of the hydraulic conductivity distribution on the flow paths, which are generally horizontal downgradient of the lagoons, but a downward component was observed in the lower half of the aquifer at the downgradient end. Simulations of recharge in the lagoons caused a rise in water table under the lagoons and a groundwater average velocity of 14 m/y was calculated in those conditions.

Results of curve fitting of transport solution to historical chloride arrival curves and tritium concentrations suggest that the liquid disposal in the early years of operation at the site are the source of the plume observed today. This plume behaves as a slug migrating downgradient at a velocity less than 30 m/y, and disperses in the aquifer. Along the cross-section A-A', unretarded species have reached a zone of downward migration while retarded species have not and are still in the zone of horizontal migration.

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**THE ECONOMIC BENEFITS OF PREVENTING
GROUNDWATER CONTAMINATION.**

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University, Lansing, Michigan.

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ASSESSMENT OF OVERLAND FLOW
BIOLOGICAL TREATMENT TECHNOLOGY
FOR REMOVAL OF ORGANIC COMPOUNDS FROM GROUNDWATER

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ABSTRACT

This study, funded in part by the Ministry of the Environment, provides an assessment of the performance of an overland flow, biological treatment process to effectively reduce levels of organic compounds in contaminated groundwater to acceptable concentrations for discharge to receiving water bodies. A gasoline spill in Delta, Ontario has contaminated the local bedrock and overburden aquifers. Remedial work entailed the installation of a purge well and operation at a flow rate of 360 L/S. Low but carcinogenic levels of benzene and PAH compounds in the purge well effluent required treatment prior to surface water discharge. Low cost overland flow, biological treatment technology rather than conventional treatment technology was implemented to reduce contaminant levels prior to surface water discharge. The paper provides details of the construction of the overland flow, biological treatment system and a preliminary assessment of the performance of the system during the first six months of operation. Benzene at concentrations of 100-150 ug/L, toluene at 10-30 ug/L, ethylbenzene at 90-150 ug/L, xylene at 80-230 ug/L and naphthalene at 30 ug/L are characteristic contaminant concentrations in the purge well effluent. At the outlet of the treatment system, contaminant concentrations are generally at or below laboratory detection levels (1 ug/L).

ASSESSMENT OF OVERLAND FLOW, BIOLOGICAL TREATMENT TECHNOLOGY FOR REMOVAL OF ORGANIC COMPOUNDS FROM GROUNDWATER, R. Woeller, J.F. Devlin, D.P. Smith, Water and Earth Science Associates Limited, Box 430, Carp, Ontario, D. Cook, Ontario Ministry of the Environment, Kingston, Ontario, T. Mosquin, Mosquin Bioinformation Ltd., Lanark, Ontario.

Introduction

The rehabilitation of aquifers which have been contaminated with organic compounds is a new and important science in Ontario. Many of the hydrogeology, geochemistry and engineering principles which now permit us to clean up groundwater supplies have only been developed within the last five years. Much of the existing technology was developed for other types of wastewater treatment however, and is extremely expensive or technically unsound when applied to groundwater rehabilitation problems.

The purpose of this study was to field test the application of purge well and biological treatment technology on the remediation of contaminated aquifers. If successful, the remedial work would reduce the levels of organic compounds, in a seriously contaminated groundwater aquifer, to existing drinking water standards and demonstrate the effectiveness of overland flow/biological treatment. The organic compounds of particular concern in this situation were aromatic volatile organic compounds (such as benzene).

The methods tested in this report should be applicable to a wide range of groundwater rehabilitation problems associated with spills, landfill operations and remedial undertakings. However, the research to date is solely applicable to gas spill problems.

2. Background

Delta, Ontario, is located between Upper and Lower Beverly Lakes, along Highway 42, about 50 km northeast of Kingston (Figure 1). The first indication that a groundwater contamination problem existed in Delta came in 1976 when a resident complained to the Ministry of the Environment (MOE) that her water had acquired a petroleum taste and odour. After this complaint, a gasoline audit was carried out at the service station located immediately across the road (northward) from the contaminated well (Figure 2). A deficit of 400-4500 litres (900-1000 gallons) of regular gasoline was discovered and shortly afterward the suspect tank was pressure tested. Ultimately, it was discovered that a loose fitting on the underground storage tank suction line was leaking a small volume of fuel each time the tank was filled.

The MOE conducted a field investigation of the site, in June, 1976, and concluded that the service station was the source of contamination. An activated carbon filtration treatment system was installed in the affected residence.

In 1980, a second case of groundwater contamination was reported to the MOE. This complaint came from the homeowners living immediately to the west of the first affected well. A treatment system was also installed at this location.

In 1982, Water and Earth Science Associates conducted a hydrogeological investigation of the town, as part of a preliminary engineering report for the town, under the Ministry Individual Correction Services Program. Related sampling from overburden piezometers installed downgradient of the problem area, revealed that the gasoline contamination problem was much more extensive than had previously been realized. The contaminant plume was estimated to be 500 m long, 350 wide and 60 metres deep (based on taste and odour thresholds). It was estimated that, overall, between 7700 and 3400 litres (1700 - 7500 gallons) of fuel had been lost, and an estimated 173 million litres (38 million gallons) of groundwater were polluted. Treatment units were supplied to all homeowners as soon as the presence of hydrocarbons became apparent in their water.

3. Site Description

3.1 Geology

The Hamlet of Delta is located on the eastern margin of the Frontenac Axis which is a physiographic subregion of the Precambrian Shield. This section of the axis comprises carbonate metasedimentary rocks with the predominant rock types being marble and skarn (Figure 3).

Nepean sandstone unconformably overlies the marble in the northern portion of the town. Marble is present at surface in near the centre of the hamlet, on the banks of the Delta Creek,

Surficial materials, in the northern portion of the hamlet, include a sequence of sands and gravels overlain by a lacustrine clay and silt. The sand and gravel sequence (glaciofluvial) comprises a coarse gravel (overlying bedrock), overlain by finer gravels, coarse sands and fine grained silty sand. The overburden thickness varies considerably across the site; the sand and gravel is found in depressions in the bedrock surface.

3.2 Drainage

Delta Creek runs through the centre of the hamlet and connects Upper and Lower Beverly Lakes. The creek exhibits a

seasonably variable flow which can be very low in the summer months.

Foundry Creek flows along the west side of the study area and shows a similar discharge cycle to that of Delta Creek. Foundry Creek appears to be fed by groundwater from the sand and gravel deposits through which it has cut its path.

4. Methods of Study

An assessment of various remedial technologies was undertaken to determine a feasible approach to remediation of the groundwater aquifer. The assessment indicated that a purge well system, in conjunction with an overland flow biological treatment facility, was the most cost effective approach to cleanup. Aquifer testing indicated that the plume could be controlled by operating one or two purge wells at a total discharge rate of no more than 11.4 L/sec (150 GPM). Subsequently, the design of a low cost biological treatment system, consisting of a surface aeration unit, iron/organic precipitation channels where biological renovation of the discharge would occur and a marsh treatment area for effluent polishing.

4.1 Treatment Field Design

The construction phase was initiated in the late fall and winter of 1986 and was concluded during January 1987. A 200 mm diameter purge well, 43 m in depth, was installed along the north boundary of the treatment facility. The purge well was situated where piezometer and private well sampling had indicated the greatest contamination to be, and was operated with a 14 horsepower submersible turbine pump requiring low maintenance. The groundwater discharge was directed to two concrete sprinkler basins: one emptied onto a gently sloping grass field (A field), and the other into three treatment channels containing various types of wetland vegetation (BA, BB, BC) (Figure 4).

At each sprinkler basin, a 5-7.4 cm diameter PVC header pipe is outfitted with small diameter, vertical, steel outlet nozzles located every at intervals along its top side. As the groundwater is pumped through these assemblies it is forced through the nozzles and produces a fan shaped "sprinkler" effect. The purpose of aeration is to promote contact of the discharge water with the air, thereby stripping the volatile fraction of the organic contaminants from the water. At the foot of each sprinkler basin, coarse gravel has been spread to form a rip rap structure. This feature is designed to maximize the physical agitation of the contaminated water, provide an increased contact surface area and therefore maximize its exposure to the air.

The grass field (A) was designated an "overland flow" field. It was prepared by spreading topsoil over the existing soil,

grading uniformly to a 2% slope, and then rototilling, fertilizing and seeding the field. The grasses chosen to grow include Phalaris arundinacea (Reed Canary Grass), Glyceria grandis (Manna grass) and Calamagrostis canadensis (Bluejoint). Flow depth raises with location on the field but averages between 1-2 cm.

Field B comprises three channels, each containing different kinds of vegetation. The first channel (A) was filled with baled hay to a depth of 20 cm. This channel provides information about the attenuation potential of decaying vegetation. The second channel (B) was seeded with Hydrocharis morsus-ranae (Frog-bit), a floating and strongly stoloniferous species. These plants have the characteristic of forming extensive, fibrous roots which hang downward in the water. The third channel was vegetated with narrow leaved emergent plants (mainly grasses). The principal species planted include Calamagrostis canadensis (Bluejoint), Phalaris arundinacea (Reed Canary Grass), and Poa palustris (Swamp Meadow Grass).

The treated discharge water is collected in an artificially created marsh containing cattails, Frog-bit, Lythrum salicaria, Carex crinellii, Sagittaria cuneata (Arrowleaf), Cicuta bulbifera (Bulb-bearing Water Hemlock), Alisma plantago aquatica (Water Plantain) and some others. Water ultimately drains from the marsh into Foundry Creek.

4.2 Monitoring Program

Samples have been collected from three sources to monitor the status of the contaminant plume and the performance of the treatment facility: (1) All private wells within the affected area were sampled semi annually; selected wells were sampled quarterly, (2) a suite of samples, comprising untreated groundwater and water from various distances along the treatment channels, have been collected at the treatment field biweekly, (3) groundwater samples have been collected from the piezometers installed in the shallow overburden. The latter source was only monitored during the intensive plume definition phases of the project.

Analyses were conducted by laboratories specializing in the required aspects. Bondar Clegg and Company Limited was used for inorganic analyses and phenols, Dr. John Poland of Queen's University was employed for volatile organic and some inorganic analyses, and Mann Testing Laboratories was employed for specialized PAH analyses.

Between July 27 and August 7, 1987, a thorough study of the treatment field and the status of the plume was conducted. Water and Earth Science Associates carried out the sampling program in conjunction with Ministry personnel from the Kingston District

Office. The Mobile Organic Laboratory Trace Organic Section of the Ministry's Laboratory Service Branch was situated on site during the evaluation to provide the necessary laboratory support for the volatile organic analyses. In addition, laboratory support for the analysis of other parameters was provided by the Ministry Central Laboratory, the Kingston Laboratory and Queen's Laboratory.

Within the treatment facility, samples were collected along the lengths of the grass field and the treatment channels. The parameters of interest included conductivity, alkalinity, calcium, magnesium, sulfate, nitrate, nitrite, ammonia, phosphorus, COD, BOD, trace metals, polyaromatic hydrocarbons, volatile hydrocarbons and phenols. In addition, flow cell measurements were carried out along the hay filled treatment channel (BA). These measurements determined temperature, O₂ concentration, EH, and conductivity.

4.3 Sampling Methods

Samples for volatile organic analyses were collected without headspace in 100 ml glass bottles and sealed with Teflon septa. The collection procedure involved filling the bottles with the sample tubing inside so that sample/air contact was minimized. After 6 rinses with the solution being sampled, the bottles were allowed to overflow for several minutes. Finally, the sample tubing was slowly withdrawn leaving a bubble of water protruding from the bottle necks. The bottles were then quickly capped and stored at or below 4 degrees centigrade in a cooler with ice.

Samples for extraction were collected in 1 L amber glass bottles, and sealed with foil lined caps. The collection procedure involved filling the bottles with the sample tubing inside. After 6 rinses with the solution being sampled the bottles were allowed to fill to within a few millilitres of the top. The foil liners were washed (with HPLC grade methanol and the solution being sampled) and placed over the bottle neck. Finally, the caps were tightened in place and the bottle placed in a cooler with ice and stored at a temperature of less than 4 degrees centigrade.

Samples collected for major cation and anion analysis were stored in either polyethylene or glass (1L) and were kept cool until their arrival at the laboratory. Samples collected for metals analysis were first filtered through a 0.45 um membrane and then acidified with nitric acid.

4.4 Flow Cell Measurements

A Canlab combination pH electrode was standardized in pH 4, 7 and 10 buffers for field pH measurement; a platinum electrode was standardized in a ferrous/ferric solution (Light,

1972) for field EH measurement. Sampling tubes were connected to a peristaltic pump which was, in turn, connected to the flow cell. The cell contained the standardized pH, and EH probes as well as a conductivity/temperature probe. Pumping at each site was continued until all readings stabilized (this generally required 10 minutes once the flow cell was full). The readings were then recorded, the flow cell disassembled and washed with distilled water, the probes restandardized and the system set up at a new location.

All tubing and filtering equipment was washed by rinsing several times with distilled water, then with a 50% solution of nitric acid, followed by several more rinses with distilled water. In addition, the system was flushed with the solution to be sampled for 10 minutes, prior to collecting a sample, to prevent carry-over of dissolved material between sampling locations. In general, the cation and anion samples were collected after the flow cell measurements were completed, so that the operator could be certain representative samples were obtained.

5. Results and Discussion

5.1 Private Wells

Many of the contaminated wells in Delta are completed in the bedrock, at depths between 13 and 40 metres. A few shallow dug wells were also contaminated, but these tend to be located near the source area.

Among the components of gasoline which constitute the greatest threat to health benzene, an aromatic, was found to be the one most consistently present in high concentration in ground-water from private wells. The highest concentrations of benzene were encountered at the homes located most directly southwest of the service station where the leak occurred, along the north side of Highway 42 (500-1000 ppb, Figure 2). Most homes were much less severely affected, with benzene concentrations ranging between 10 and 200 ppb. This was the situation as it existed at the time the treatment field began operation.

Seven months after the purge well was switched on, 59 million litres of contaminated water had been pumped and none of the private wells within the affected area had concentrations of benzene above the World Health Organization drinking water guideline limit, 10 ppb. Table 1 summarizes the benzene concentrations which were measured at the affected homes between 1985 and 1987. In fact, none of the common aromatic constituents of gasoline were present above trace levels (Table 2). Only some of the odiferous, aliphatic compounds remained detectable. Figure 5 shows that although the pumping has reduced benzene, toluene

and xylene levels by an order of magnitude (>300 ppb to <30 ppb), aliphatic hydrocarbons are still present in the groundwater.

The purge well at the treatment site was completed in the most contaminated section of the bedrock aquifer. Consequently, gasoline contamination is still apparent there. However, the improvement in the condition of the aquifer is apparent in Figure 6. The concentrations of all the major aromatic contaminants show a steady decline in concentration between January and August, 1987. At the present rate of improvement, the purge well itself will be contaminant free by September 1988. However, it is anticipated that as the contaminant levels drop with time, tailing will occur and as a result total cleanup will take longer.

5.2 Overburden

In July, 1987, seven months after the purge well was switched on, the contaminant concentrations in the overburden water remained between the non-detectable (<1 ppb background) and 1000 ppb. The highest concentrations were encountered between 100 and 200 metres downgradient from the source, with benzene present at 825 and 950 ppb at GD6 and GD5, respectively. Trace levels of hydrocarbons were detected at D1, 388 metres away from the source (Table 3, Figure 2). These data indicate that the purge well currently in operation within the bedrock aquifer is not effective in cleaning up the overburden aquifer. It is likely that a second purge well will be required to decontaminate the overburden aquifer.

5.3 Treatment Field

Water samples have been collected at the discharge point from the treatment field on a regular basis between April and August, 1987. The analytical results from these samples are summarized in Figure 7. With the exception of one sample collected in early spring, which was found to contain trace levels of phenols, no gasoline derived contaminants have been detected leaving the site. Figure 8 contrasts the gas chromatograms of untreated groundwater and water leaving the treatment facility. In addition, iron concentrations drop from about 2 ppm in the untreated water, to <0.1 ppm in the discharge water.

The treatment field was sampled intensely in July, 1987, to examine the effectiveness of the treatment process more thoroughly (Tables 4, 5). Sampling points were established along the flow path in both the grass field (A) and the channels (BA, BB, BC). In the grass field (A) sampling points were established by partially burying plastic drinking water cups in the field, so that the rims were at ground level. This created a series of small reservoirs for sampling purposes. Two sampling lines were

established along the length of the grass field, each having 5 sampling points. Three points along each line were within 5 m of the sprinkler basin; the two remaining points along each line were located at the midpoint and the end of the field, respectively. In each of the channels, sampling points were established by strapping one quarter inch diameter polyethylene tubing to 1/2 inch diameter PVC stocks. A filter mesh (#200) was strapped to the end of the polyethylene tubes to prevent sediment from being drawn in during sampling. Six of these sampling points were placed along the lengths of each treatment channel (Figure 4). Two points were situated near the sprinkler basin, in each case. The remaining four were situated with increasing spacing along each channel length. In addition, samples were collected at the exit of each channel.

A. Inorganic Chemistry: Along the length of the grass field, COD and BOD were found to be relatively constant (10 and 0.6 ppm, respectively). However, some trends were noted in data from the treatment channels. Along channel BA (hay filled), the COD was observed to rise sharply from 5 to 24 ppm 14 m from the source, and BOD rose gradually from 0.25 ppm at the source, to 1.3 ppm at the end of the channel (Table 4, Figure 9). These data indicate that organic matter, from the hay and soil lining the channel, is being dissolved.

Flow cell measurements gathered along channel BA indicate that the most notable changes to the water chemistry occur during the sprinkler phase of treatment. Dissolved oxygen concentrations increase sharply from <2 ppm at source to ~9 ppm at the base of the rip rap. A corresponding increase in the EH was also observed (rise from 69 mv to >300 mv). The water temperature was observed to rise from 13 C at the source to 22 C after the sprinklers.

As the water flows through the channel, dissolved oxygen and EH were found to increase marginally for a distance of about 30 m from the source. Beyond this distance, both parameters were observed to decrease; at the discharge point from channel A oxygen was present at a concentration of 5.4 ppm, EH was found to be 229 mv (Figures 9 & 10). A similar trend was observed in the temperature measurements. A maximum temperature of 28 C was reached at a distance of about 66 m from the source. Beyond this point, temperature dropped slightly to 26 C at the discharge point. The temperature changes are probably the result of shadows cast across the lower end of the treatment channel on the day of the measurements. The changing oxygen concentration and EH may be directly due to the increasing BOD along the channel length.

The only parameter which showed a systematic increase along the entire length of the channel was conductivity (as measured in the flow cell). Near the source, the conductance was measured at

270 umhos, while at the discharge point it found to be 700 umhos (Figure 10). This rise is most likely due to dissolved organic matter since the major inorganic ionic species show no appreciable change in concentration but COD increases significant along the channel length. Conductivity measurements conducted at the MOE laboratory (Kingston) do not reflect a similar trend. All the laboratory values are >900 umhos. The reason for this discrepancy has not been identified at this point in time.

In general, there are no significant changes to the concentrations of the major ionic species in the water as it flows across the grass field or through the treatment channels. Hardness is between 330 and 390 ppm (CaCO₃), total nitrogen does not exceed 0.15 ppm, alkalinity was measured to be between 240 and 360 ppm (CaCO₃), sulfate is present between 39 and 43 ppm, and phosphorus is only detectable in trace quantities. Only iron concentrations have been shown to change during treatment. At source, levels are about 2 ppm; at discharge the concentration is <0.05 ppm. Most of the iron removal seems to occur near the rip rap, based on the severe staining on the cement basin and the gravel.

B. Organic Chemistry: The organic contaminants considered in this study are listed in Table 5. The concentrations of these contaminants at various distances along the grass field and the treatment channels are also presented in Table 5 and shown graphically in Figures 11&12. These data demonstrate that the attenuation of the organic contaminants occurs almost entirely within the first few metres of the rip rap.

Contaminant concentrations in the water filling the cement basins, and at the base of the rip rap in field A (grass field) are about one quarter of those measured in the untreated water (benzene was measured at 20 ppb in the trench and 80 ppb at source; ethylbenzene was measured at 16 ppb in the trench and 51 ppb at source; xylene was measured at 3 ppb in the trench and 9 ppb at source). These data indicate that the sprinkler aeration system is responsible for approximately 75% removal of volatile contaminants. Three metres away from the rip rap levels of all contaminants except benzene are below analytical detection limits (1 ppb). Benzene is present in trace amounts for only a few metres beyond that (Figure 11).

Low levels of bromodichloromethane and trichloroethylene were reported in the untreated water at the treatment site (A trench 11 ppb and BT 10 ppb). These analyses were carried out by GC only, with no verification by mass spectrometry. Discussions with laboratory personnel indicate that such results may be due to impurities introduced by labware. These contaminants are not considered to be indicative of the contamination in the groundwater, since previous priority pollutant scans have not revealed the presence of these compounds.

6. Conclusions

The following conclusions may be drawn from the work conducted in this study:

- 1) Overland biological treatment of groundwater is an effective method for cleaning up gasoline contaminated groundwater (dissolved phase), and for removing most of the iron associated with the hydrocarbon plume.
- 2) Throughout the spring and summer, 1987, the quality of the discharge water remained high and no significant (contaminant related) stress was observed in the vegetation. Thus, preliminary results indicate the system is suitable for long term treatment.
- 3) The treatment facility at Delta could be scaled down considerably and maintain its effectiveness in cleaning up groundwater contaminated with gasoline. Most of the removal of hydrocarbon and iron appears to be taking place in the first few metres.
- 4) Within a very short time period (seven months) all wells within a few hundred metres of the purge well (and completed in bedrock) have experienced improvement in water quality. None of the formerly contaminated private wells contain volatile aromatic organics at more than trace levels (1-4 ppb). All values are within the MOE drinking water guideline limits. Some odour persists in water from the homes which were most severely affected in the past, however, this problem is likely the result of low levels of aliphatic hydrocarbons for which no drinking water limit has been set.
- 5) No significant differences were observed in the attenuating properties of hay, Frog-bit, or wetland grasses.
- 6) Approximately 75% of volatile contaminants may be removed from water through the use of a sprinkler system (for contaminant levels between 50 and 100 ppb).
- 7) The purge well is effectively cleaning up the bedrock aquifer, but not the overburden aquifer. It is likely that a second purge well, completed in the overburden, will be necessary before the site can be restored.
- 8) The rehabilitation of groundwater by purge well and biological treatment is effective at a fraction of the cost of conventional methods.

Acknowledgements

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The Research Advisory Committee of the Ontario Ministry of the Environment is acknowledged and thanked for their financial support for the data analysis and production of this report.

BENZENE CONCENTRATIONS OVER TIME, DELTA HOMES

Table 1:

Sampling performed by Water and Earth Science Associates

Analyses performed by Queen's University, MCE Analytical Laboratory, Zeneca Environmental, Mana Testing

Blanks = not analyzed or not sampled; 0 = not detected

Lat	Name	Depth	System	7-20-87	8-10-87	8-15-87	8-14-87	8-1-88	8-12-88	2-26-88	1-7-88	11-11-88	1-9-89	7-22-89	5-14-89	5-15-89		
		(ft)		unfilt.	filt	unfilt.	filt	unfilt.	filt	unfilt.	filt	unfilt.	filt	unfilt.	filt	unfilt.		
11				1	1	1	1	1	1	1	1	1	1	1	1	1		
12				1	1	1	1	1	1	1	1	1	1	0.2	1	1		
13 Steary				1	0	1	1	1	1	1	1	1	1	0.1	1	0.3		
14 Vollich		13.7		1	0	0	0	0	0	0	0	0	0	0.1	1	0.5		
15 B. Pratt				1	0	0	0	0	0	0	0	0	0	0.3	1	1		
16				1	0	1	1	1	1	1	1	1	1	1	1	1		
17 L. Pratt			ACF-P	1	0	0	0	0	0	0	0	0	0	21.0	1.7	131.0	131.0	0.8
18 Halliday			ACF-P	1	3	0	1.7	1	31.9	42.6	1	1	1	84.0	0.7	1	1	
19 Jacques		29.0	ACF-P+0	0	0	2.8	1	0.0	16.0 ^a	0.0	1	1	1	0.1	0.4	1	0.5	
20 Donald			ACF-S+0	0	0	2.8	1	28.0	133.0	0.0	1	1	1	1	1	1	1	
21 Price		9.1	ACF-P+0	0	0	0	0	0	142.0	1	2.5	1	1	1	0.9	1	0.5	0.5
22 Grant				1	0	1	1	1	1	1	1	1	1	0.5	1.8	1	1	
23 Ayres				0	0	1	1	1	1	1	1	1	1	0.2	1.0	1	1	
24 Phillips		16.8	ACF-P+0	0	0	0	0	0	0	0	0	0	0	0.8	0.2	0.8	0.8	
25 Connell		27.0	HD	1	0	1	1	7.5	1	1	1	1	1	74.0	1	84.0	1	
27 Pratt Apt		24.4	ACF	1	6	1	4.2	1	3.8	27.0	5.0	1	1	1	0.7	22.0	1	7.5
28 S. Grav		9.7		0	0	1	1	1	1	1	1	1	1	1	0.8	1.2	1	0.5
29 French				0	0	0	0	0	0	0	0	0	0	1.4	1.2	1.2	1	
30 Cook			ACF	0	0	0	0	0	0	0	0	0	0	1.0	1.2	26.0	1	
31 Ely			Ban	0	0	0	0	0	0	0	0	0	0	6.1	6.8	6.8	0.5	
32 Greene		14.4	HD	1	0	1	1	0.0	1	2.1	4.5	0.4	1	8.2	5.7	1.1	1	
43 EDCCL-3			ACF-1	0	0	0	0	0	0	0	0	0	0	2.0	1.3	2.1	7.8	0.8
44 EDCCL-21			ACF-1	0	0	0	0	0	0	0	0	0	0	2.0	1.3	2.1	7.8	0.8
45 Latson		15.7	ACF	0	0	0	0	0	0	0	0	0	0	123.0	155.0	92.0	1.9	42.0
46 Akens		1.0		1	0	1	1	1	1	1	1	1	1	0.1	1	1	1	
47 E. Grav			ACF	1	0	0	0	0	0	0	0	0	0	0	21.8	1		
48 Vergeront			ACF	0	0	0	0	0	0	0	0	0	0	0	0	0	0.5	
49 Wilson		5.0		0	0	0	0	0	0	0	0	0	0	0.1	0.1	0.1	0.1	
50 Ains			all ACF	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
51 All.		0.4		0	0	0	0	0	0	0	0	0	0	0	0.1	0.1	0.1	
52 Vollich		12.1		0	0	0	0	0	0	0	0	0	0	0	0.1	0.1	0.1	
53 J. Jones				0	0	0	0	0	0	0	0	0	0	0	0.1	0.1	0.1	
54 Sturzaker		21.0		0	0	0	0	0	0	0	0	0	0	0	0.1	0.1	0.1	
55 Russell		23.0		0	0	0	0	0	0	0	0	0	0	0	0	0	0	
56 W.M.P.		50.1		0	0	0	0	0	0	0	0	0	0	1.1	1.1	1.1	0.1	
57 Bravelle				0	0	0	0	0	0	0	0	0	0	0	0	0	0	
58				0	0	0	0	0	0	0	0	0	0	0	0	0	0	
59 Willard				0	0	0	0	0	0	0	0	0	0	0	0	0	0	
60				0	0	0	0	0	0	0	0	0	0	0	0	0	0	
61 Gray				0	0	0	0	0	0	0	0	0	0	0	0	0	0	
62 Library				0	0	0	0	0	0	0	0	0	0	0	0	0	0	
63 Russell				0	0	0	0	0	0	0	0	0	0	0	0	0	0	
64 Schuster		15.2		0	0	0	0	0	0	0	0	0	0	0	0.1	0.1	0.1	
65 RED 1 east		23.0		0	0	0	0	0	0	0	0	0	0	1.0	1.0	1.0	0.1	
66 LIQUOR STORE				0	0	0	0	0	0	0	0	0	0	0	0.1	0.1	0.1	

Table 1: RESULTS OF THE PIEZOMETER SAMPLING PROGRAM, DELTA, SUMMER, 1967
 Sampling conducted by Water and Earth Science Associates
 Analyses performed by RGE (Mobile Laboratory)
 Blanks = no analysed or not sampled; 0 = not detected

Loc	Elev. s.d.s.l.	Depth (m)	111TCFA	BENZ	TOL	TECEE	ETHERE	<i>n</i> -MYL	<i>m</i> -MYL	CHLCS	COL4	111TCFA	CLSENY	CHERS	1122TCFA	INCLOENE	11222BENX	BACLOON	PHEN TCEE
601-1	89.85	7.62																	
601-2	90.75	6.71																	
601-3	92.59	4.88																	
601-4	94.12	3.03																	
602-1	84.47	12.09																	
602-2	85.97	10.59																	
602-3	87.47	9.39																	
602-4	88.77	7.39																	
602-5	90.47	6.39																	
603-1	84.22	12.32																	
603-2	85.62	10.22																	
603-3	87.32	8.32	0	116	168	0	221	23	164	0	0	0	0	0	0	0	0	0	
603-4	88.52	7.52																	
603-5	90.22	6.02	0	46	20	0	122	18	30										
621-1	85.34	11.42																	
621-2	84.31	10.42																	
621-3	82.11	12.18	0	950	0	0	0	0	0										
621-4	84.11	11.48																	
621-5	85.11	10.38																	
621-6	86.11	9.18																	
621-7	87.11	8.18																	
621-8	88.11	7.18																	
621-9	89.11	6.18																	
621-10	90.11	5.09	0	522	0	1	10	9	0										
621-11	91.11	4.39																	
621-12	92.11	3.38																	
621-13	93.11	2.38																	
621-14	94.11	1.38																	
621-15	95.11	0.38																	
621-16	96.11	0.38																	
621-17	97.11	0.38																	
621-18	98.11	0.38																	
621-19	99.11	0.38																	
621-20	100.11	0.38																	
621-21	101.11	0.38																	
621-22	102.11	0.38																	
621-23	103.11	0.38																	
621-24	104.11	0.38																	
621-25	105.11	0.38																	
621-26	106.11	0.38																	
621-27	107.11	0.38																	
621-28	108.11	0.38																	
621-29	109.11	0.38																	
621-30	110.11	0.38																	
621-31	111.11	0.38																	
621-32	112.11	0.38																	
621-33	113.11	0.38																	
621-34	114.11	0.38																	
621-35	115.11	0.38																	
621-36	116.11	0.38																	
621-37	117.11	0.38																	
621-38	118.11	0.38																	
621-39	119.11	0.38																	
621-40	120.11	0.38																	
621-41	121.11	0.38																	
621-42	122.11	0.38																	
621-43	123.11	0.38																	
621-44	124.11	0.38																	
621-45	125.11	0.38																	
621-46	126.11	0.38																	
621-47	127.11	0.38																	
621-48	128.11	0.38																	
621-49	129.11	0.38																	
621-50	130.11	0.38																	
621-51	131.11	0.38																	
621-52	132.11	0.38																	
621-53	133.11	0.38																	
621-54	134.11	0.38																	
621-55	135.11	0.38																	
621-56	136.11	0.38																	
621-57	137.11	0.38																	
621-58	138.11	0.38																	
621-59	139.11	0.38																	
621-60	140.11	0.38																	
621-61	141.11	0.38																	
621-62	142.11	0.38																	
621-63	143.11	0.38																	
621-64	144.11	0.38																	
621-65	145.11	0.38																	
621-66	146.11	0.38																	
621-67	147.11	0.38																	
621-68	148.11	0.38																	
621-69	149.11	0.38																	
621-70	150.11	0.38																	
621-71	151.11	0.38																	
621-72	152.11	0.38																	
621-73	153.11	0.38																	
621-74	154.11	0.38																	
621-75	155.11	0.38																	
621-76	156.11	0.38																	
621-77	157.11	0.38																	
621-78	158.11	0.38																	
621-79	159.11	0.38																	
621-80	160.11	0.38																	
621-81	161.11	0.38																	
621-82	162.11	0.38																	
621-83	163.11	0.38																	
621-84	164.11	0.38																	
621-85	165.11	0.38																	
621-86	166.11	0.38																	
621-87	167.11	0.38																	
621-88	168.11	0.38																	
621-89	169.11	0.38																	
621-90	170.11	0.38																	
621-91	171.11	0.38																	
621-92	172.11	0.38																	
621-93	173.11	0.38																	
621-94	174.11	0.38																	
621-95	175.11	0.38																	
621-96	176.11	0.38																	
621-97	177.11	0.38																	
621-98	178.11	0.38																	
621-99	179.11	0.38																	
621-100	180.11	0.38																	
621-101	181.11	0.38																	
621-102	182.11	0.38																	
621-103	183.11	0.38																	
621-104	184.11	0.38																	

Table 3: RESULTS OF THE PIEZOMETER SAMPLING PROGRAM, DELTA, SUMMER, 1987
 Sampling conducted by Water and Earth Science Associates
 Analyses performed by MOE (Mobile Laboratory)
 Blanks = no analysed or not sampled; 0 = not detected

Table 4:

RESULTS OF CELTA MEASUREMENT FIELD SAMPLING PROGRAM, SUMMER, 1987

Sampling conducted by Baker and Earth Sciences Associates

Analyses performed by GSC Laboratories Chemistry at Kingston, trace metals at Toronto

Blanks = not taken or not analyzed; 0 = below detection limit

Location	Bait	Depth	Temp	CDW	pH	Lab	Eh	O ₂	MLX	HARD	Ca	Mg	S04	NO3	NO2	SO3	DSP	CDB	MD	FE MACT.	FE	TM	CU	NF
Source	(#)	(m)	(°C)	(°C)	(°C)	(m)	(mV)	(mV)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)											
	A1	0.0	54.25		90.0				323	384	99	33.4	41	0.09	0.012	0.11	0.008	0	0.3	0				
	A1	0.0	4.00	4.00	96.5				322	346	98.9	32.3	40	0.07	0.01	0.08	0	0.3	0					
	A1-1	0.0	0.00	0.00																				
	A1-2	—	0.2	0.00																				
	A1-3	—	1.0	0.00																				
	A1-4	—	4.0	0.00																				
	A1-5	—	23.0	0.00																				
	A1-6	—	45.0	0.00																				
	A1-7	—	59.0	0.00																				
	A2-1	0.0	0.20	0.20	97.3				319	341	91	32.4	40	0.07	0.008	0	0	0.3	0		P			
	A2-2	0.0	0.20	0.20	96.0				337	373	93.5	32.3	40	0.04	0.024	0	0	0.3	0		0.7	0		
	A2-3	0.0	0.30	0.30	96.0				333	387	98.7	34	41	0	0.002	0.01	0.01	0.01	0.01	0.01	0	0.7	0	
	A2-4	0.0	0.20	0.20	95.2				316	328	89	36.7	37	0	0.008	0.013	0.012	0.012	0.012	0.012	0	0.4	0	
	A2-5	0.0	0.20	0.20	94.0				317	319	82.4	27.6	40	0	0.042	0.043	0.012	0	0.012	0	0.5	0		
	A2-6	0.0	0.20	0.20	91.5				297	322	78.9	37.3	39	0	0.002	0.015	0	0	0.4	0				
	A2-7	0.0	0.20	0.20	91.5				296	348	91.3	36.1	39	0.07	0.012	0.11	0	0.12	0	0.8	0			
	A2-8	0.0	0.20	0.20	97.5	8.5	8.9	1.8	310	348	91.3	36.1	39	0.07	0.012	0.11	0	0.12	0	0.8	0			
	A3-1	0.0	0.20	0.20	96.2				320	340	88.2	33.9	40	0.09	0.079	0.023	0.032	0.032	0	0.25	0			
	A3-2	0.0	0.30	0.30	97.0				325	344	83.2	31.3	41	0.05	0.025	0.033	0.033	0.033	0	0.43	0			
	A3-3	0.0	0.20	0.20	97.0				326	344	83.2	31.3	41	0.09	0.038	0.033	0.033	0.033	0	0.4	0			
	A3-4	0.0	0.20	0.20	97.0				325	349	88.7	33.3	41	0.05	0.025	0.032	0	0.032	0	0.4	0			
	A3-5	0.0	0.20	0.20	97.0				314	329	88.7	33.3	41	0.05	0.025	0.032	0	0.032	0	0.4	0			
	A3-6	0.0	0.20	0.20	96.0				326	344	83.2	31.3	41	0.09	0.038	0.033	0.033	0.033	0	0.4	0			
	A3-7	0.0	0.20	0.20	96.0				325	344	83.2	31.3	41	0.05	0.025	0.032	0	0.032	0	0.4	0			
	A3-8	0.0	0.20	0.20	96.0				326	344	83.2	31.3	41	0.09	0.038	0.033	0.033	0.033	0	0.4	0			
	A3-9	0.0	0.20	0.20	96.0				325	344	83.2	31.3	41	0.05	0.025	0.032	0	0.032	0	0.4	0			
	A3-10	0.0	0.20	0.20	96.0				326	344	83.2	31.3	41	0.09	0.038	0.033	0.033	0.033	0	0.4	0			
	A3-11	0.0	0.20	0.20	96.0				325	344	83.2	31.3	41	0.05	0.025	0.032	0	0.032	0	0.4	0			
	A3-12	0.0	0.20	0.20	96.0				326	344	83.2	31.3	41	0.09	0.038	0.033	0.033	0.033	0	0.4	0			
	A3-13	0.0	0.20	0.20	96.0				325	344	83.2	31.3	41	0.05	0.025	0.032	0	0.032	0	0.4	0			
	A3-14	0.0	0.20	0.20	96.0				326	344	83.2	31.3	41	0.09	0.038	0.033	0.033	0.033	0	0.4	0			
	A3-15	0.0	0.20	0.20	96.0				325	344	83.2	31.3	41	0.05	0.025	0.032	0	0.032	0	0.4	0			
	A3-16	0.0	0.20	0.20	96.0				326	344	83.2	31.3	41	0.09	0.038	0.033	0.033	0.033	0	0.4	0			
	A3-17	0.0	0.20	0.20	96.0				325	344	83.2	31.3	41	0.05	0.025	0.032	0	0.032	0	0.4	0			
	A3-18	0.0	0.20	0.20	96.0				326	344	83.2	31.3	41	0.09	0.038	0.033	0.033	0.033	0	0.4	0			
	A3-19	0.0	0.20	0.20	96.0				325	344	83.2	31.3	41	0.05	0.025	0.032	0	0.032	0	0.4	0			
	A3-20	0.0	0.20	0.20	96.0				326	344	83.2	31.3	41	0.09	0.038	0.033	0.033	0.033	0	0.4	0			
	A3-21	0.0	0.20	0.20	96.0				325	344	83.2	31.3	41	0.05	0.025	0.032	0	0.032	0	0.4	0			
	A3-22	0.0	0.20	0.20	96.0				326	344	83.2	31.3	41	0.09	0.038	0.033	0.033	0.033	0	0.4	0			
	A3-23	0.0	0.20	0.20	96.0				325	344	83.2	31.3	41	0.05	0.025	0.032	0	0.032	0	0.4	0			
	A3-24	0.0	0.20	0.20	96.0				326	344	83.2	31.3	41	0.09	0.038	0.033	0.033	0.033	0	0.4	0			
	A3-25	0.0	0.20	0.20	96.0				325	344	83.2	31.3	41	0.05	0.025	0.032	0	0.032	0	0.4	0			
	A3-26	0.0	0.20	0.20	96.0				326	344	83.2	31.3	41	0.09	0.038	0.033	0.033	0.033	0	0.4	0			
	A3-27	0.0	0.20	0.20	96.0				325	344	83.2	31.3	41	0.05	0.025	0.032	0	0.032	0	0.4	0			
	A3-28	0.0	0.20	0.20	96.0				326	344	83.2	31.3	41	0.09	0.038	0.033	0.033	0.033	0	0.4	0			
	A3-29	0.0	0.20	0.20	96.0				325	344	83.2	31.3	41	0.05	0.025	0.032	0	0.032	0	0.4	0			
	A3-30	0.0	0.20	0.20	96.0				326	344	83.2	31.3	41	0.09	0.038	0.033	0.033	0.033	0	0.4	0			
	A3-31	0.0	0.20	0.20	96.0				325	344	83.2	31.3	41	0.05	0.025	0.032	0	0.032	0	0.4	0			
	A3-32	0.0	0.20	0.20	96.0				326	344	83.2	31.3	41	0.09	0.038	0.033	0.033	0.033	0	0.4	0			
	A3-33	0.0	0.20	0.20	96.0				325	344	83.2	31.3	41	0.05	0.025	0.032	0	0.032	0	0.4	0			
	A3-34	0.0	0.20	0.20	96.0				326	344	83.2	31.3	41	0.09	0.038	0.033	0.033	0.033	0	0.4	0			
	A3-35	0.0	0.20	0.20	96.0				325	344	83.2	31.3	41	0.05	0.025	0.032	0	0.032	0	0.4	0			
	A3-36	0.0	0.20	0.20	96.0				326	344	83.2	31.3	41	0.09	0.038	0.033	0.033	0.033	0	0.4	0			
	A3-37	0.0	0.20	0.20	96.0				325	344	83.2	31.3	41	0.05	0.025	0.032	0	0.032	0	0.4	0			
	A3-38	0.0	0.20	0.20	96.0				326	344	83.2	31.3	41	0.09	0.038	0.033	0.033	0.033	0	0.4	0			
	A3-39	0.0	0.20	0.20	96.0				325	344	83.2	31.3	41	0.05	0.025	0.032	0	0.032	0	0.4	0			
	A3-40	0.0	0.20	0.20	96.0				326	344	83.2	31.3	41	0.09	0.038	0.033	0.033	0.033	0	0.4	0			
	A3-41	0.0	0.20	0.20	96.0				325	344	83.2	31.3	41	0.05	0.025	0.032	0	0.032	0	0.4	0			
	A3-42	0.0	0.20	0.20	96.0				326	344	83.2	31.3	41	0.09	0.038	0.033	0.033	0.033	0	0.4	0			
	A3-43	0.0	0.20	0.20	96.0				325	344	83.2	31.3	41	0.05	0.025	0.032	0	0.032	0	0.4	0			
	A3-44	0.0	0.20	0.20	96.0				326	344	83.2	31.3	41	0.09	0.038	0.033	0.033	0.033	0	0.4	0			
	A3-45	0.0	0.20	0.20	96.0				325	344	83.2	31.3	41	0.05	0.025	0.032	0	0.032	0	0.4	0			
	A3-46	0.0	0.20	0.20	96.0				326	344	83.2	31.3	41	0.09	0.038	0.033	0.033	0.033	0	0.4	0			
	A3-47	0.0	0.20	0.20	96.0				325	344	83.2	31.3	41	0.05	0.025	0.032	0	0.032	0	0.4	0			
	A3-48	0.0	0.20	0.20	96.0				326	344	83.2	31.3	41	0.09	0.038	0.033	0.033	0.033	0	0.4	0			
	A3-49	0.0																						

Table 4:

Table 5: RESULTS OF VOLATILE ORGANIC SAMPLING PROGRAM FOR THE DELTA TREATMENT FIELD, SUMMER, 1987
 Sampling performed by Natar and Earth Science Associates
 Analyses performed by MDE mobile laboratory
 Blanks = not sampled or not analyzed; 0 = not detected

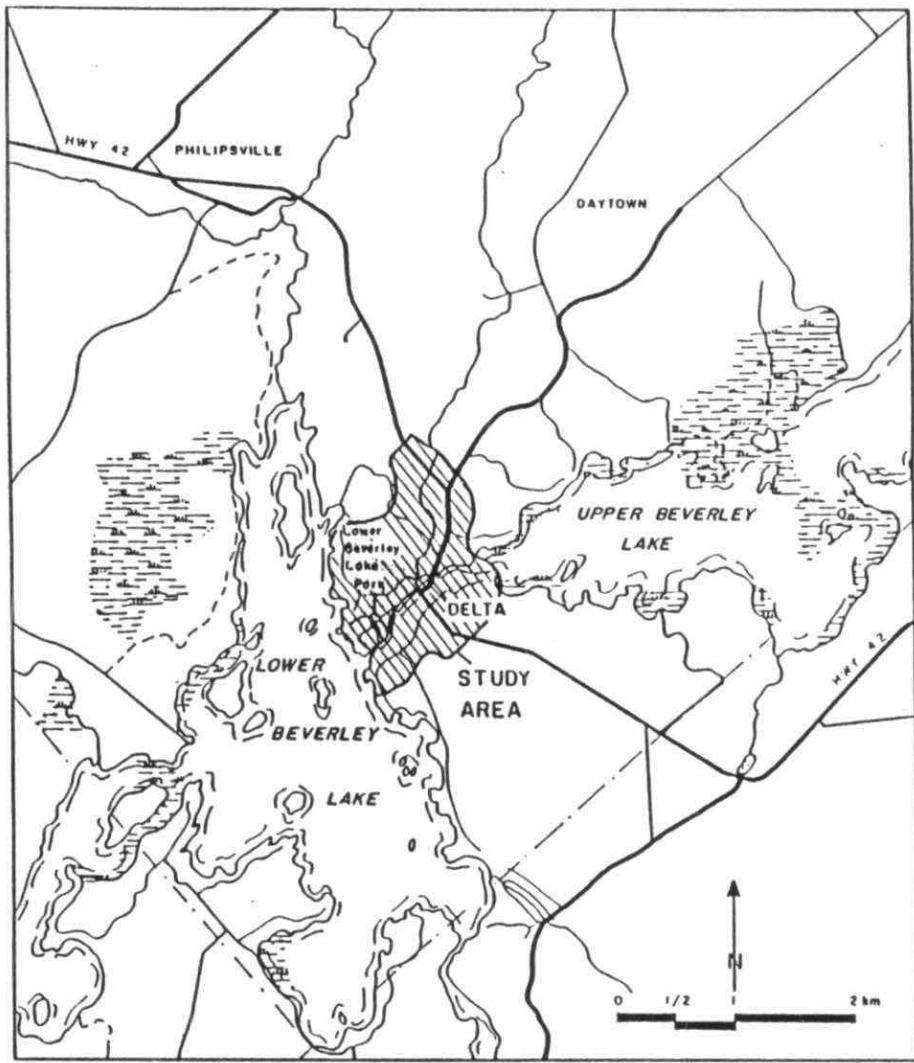


FIGURE I
LOCATION AND ACCESS MAP
HAMLET OF DELTA, ONTARIO



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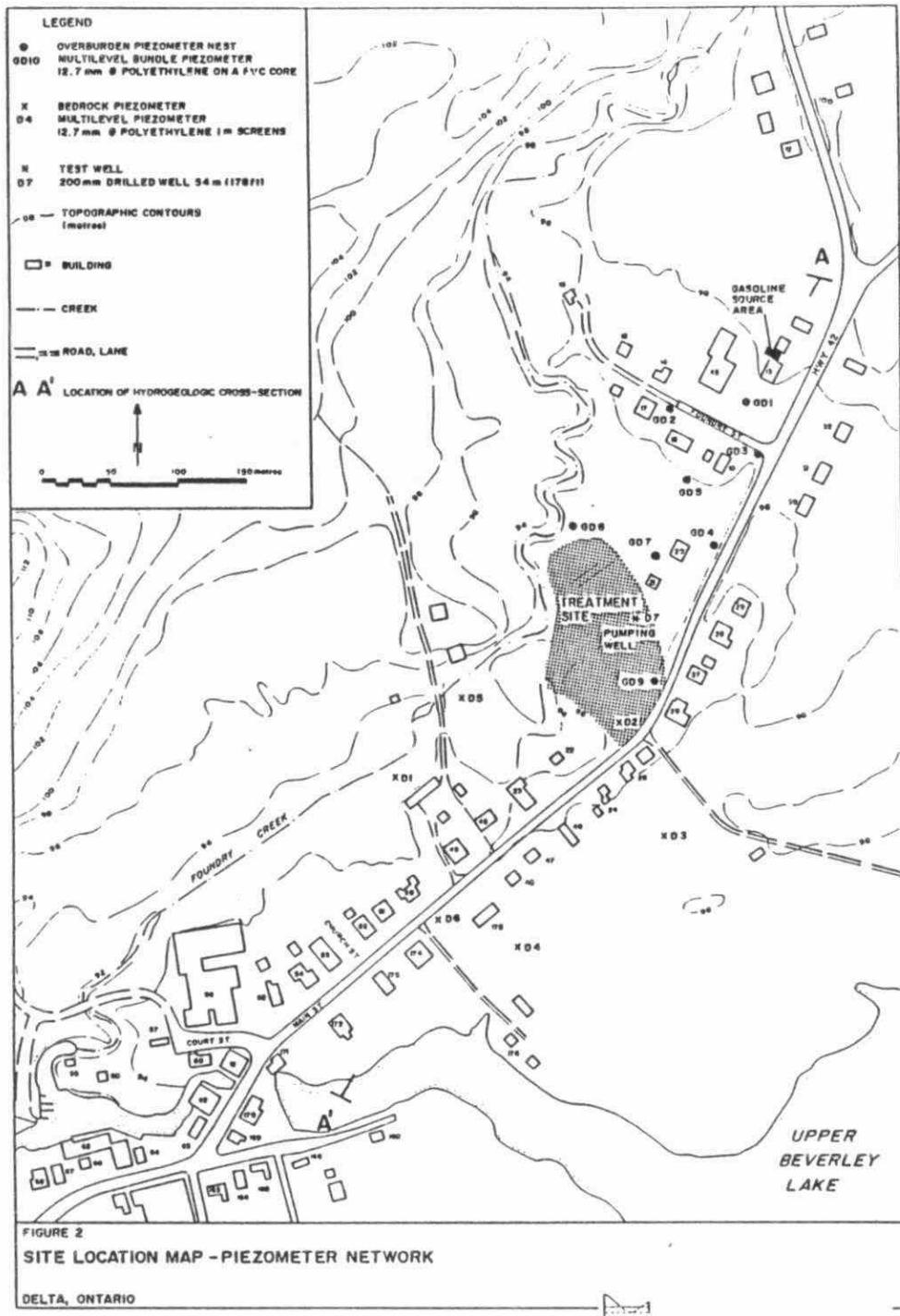


FIGURE 2
SITE LOCATION MAP - PIEZOMETER NETWORK

DELTA, ONTARIO



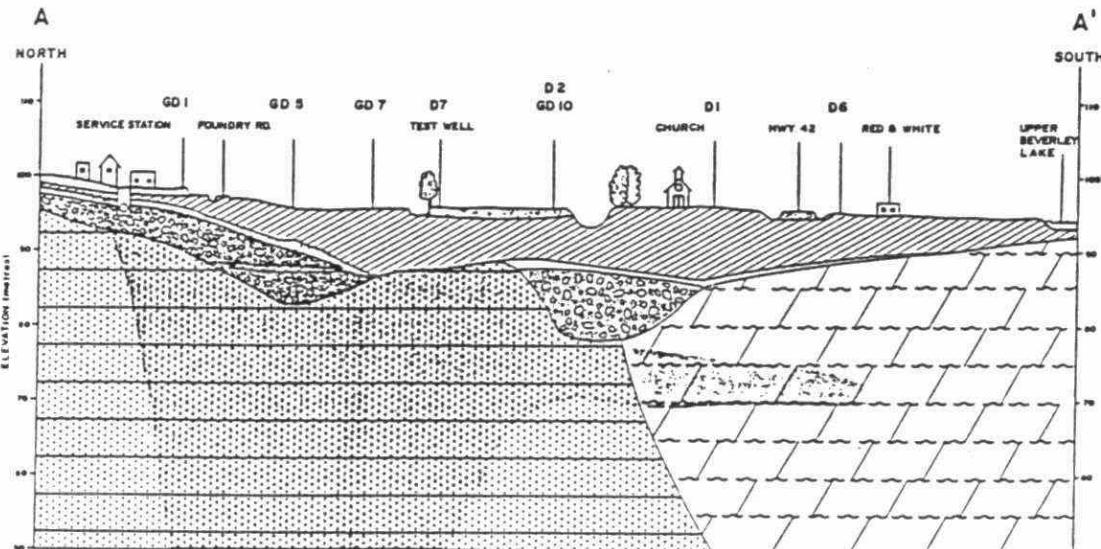
WATER AND EARTH SCIENCE ASSOCIATES LTD

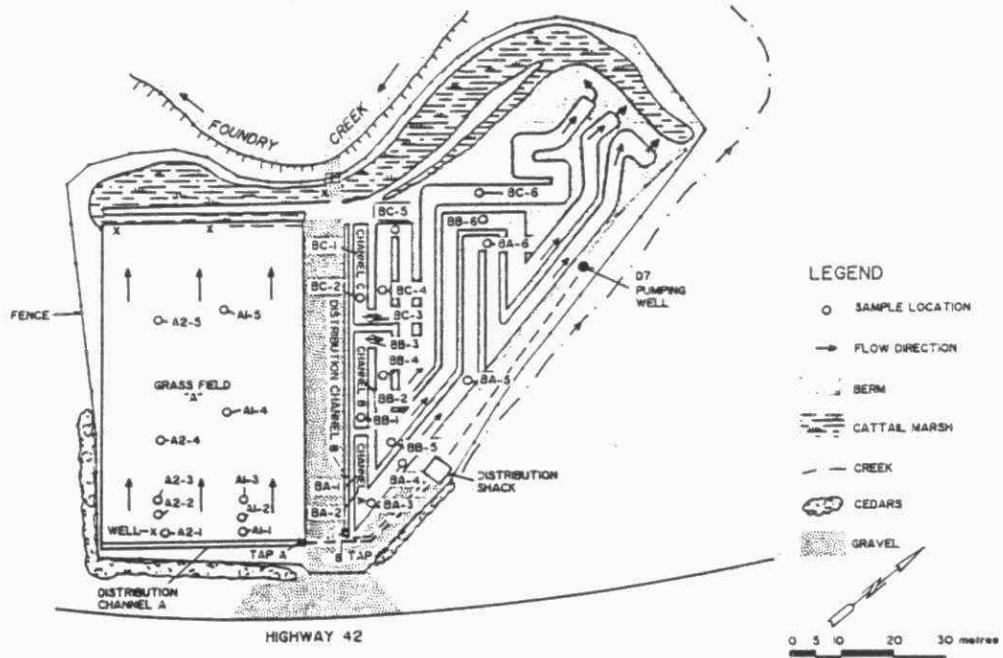
FIGURE 3
HYDROGEOLOGIC
CROSS-SECTION

DELTA, ONTARIO

LEGEND

	FILL: Sandy bouldery
	CLAY: Silty fine-grained
	SAND: Silty fine to medium grained
	GRAVEL: Pebbly with sand matrix
	SANDSTONE: Ferruginous cement
	MARBLE
	GD1 DI PIEZOMETER LOCATION
	A A' LOCATED ON FIGURE 1 ZONE OF KNOWN HYDROCARBON CONTAMINATION





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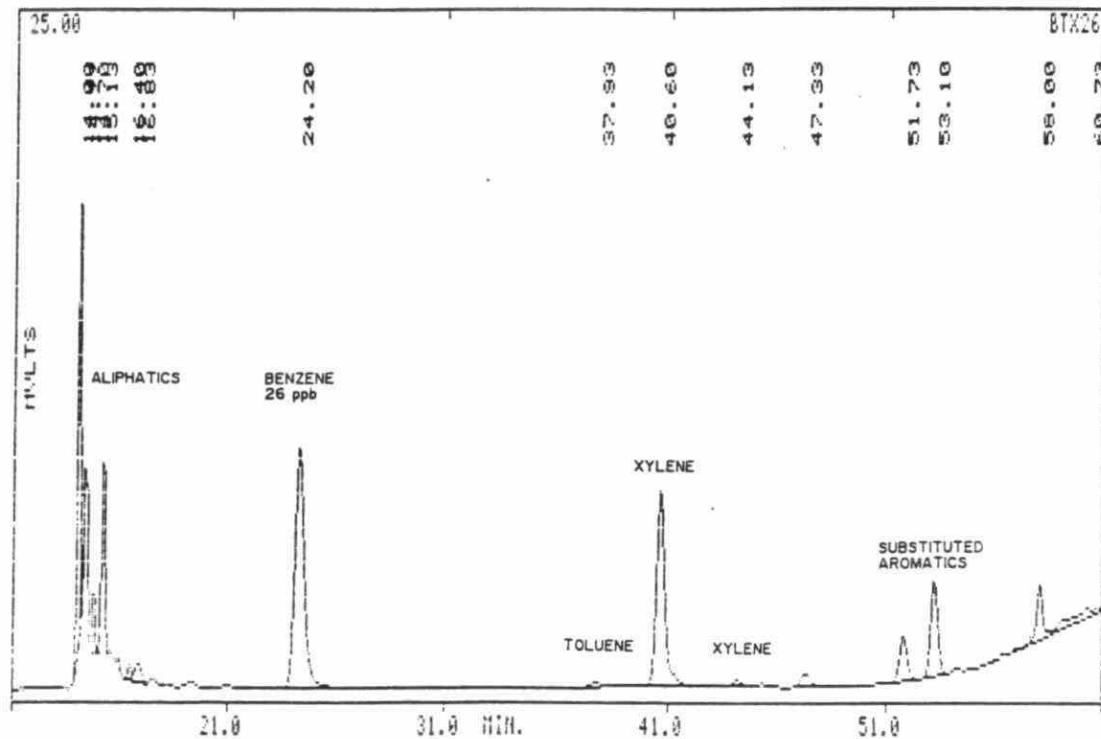


FIGURE 5
UNTREATED WATER FROM RESIDENCE ON LOT # 20



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Delta Gas Spill

Raw Water at Treatment Field

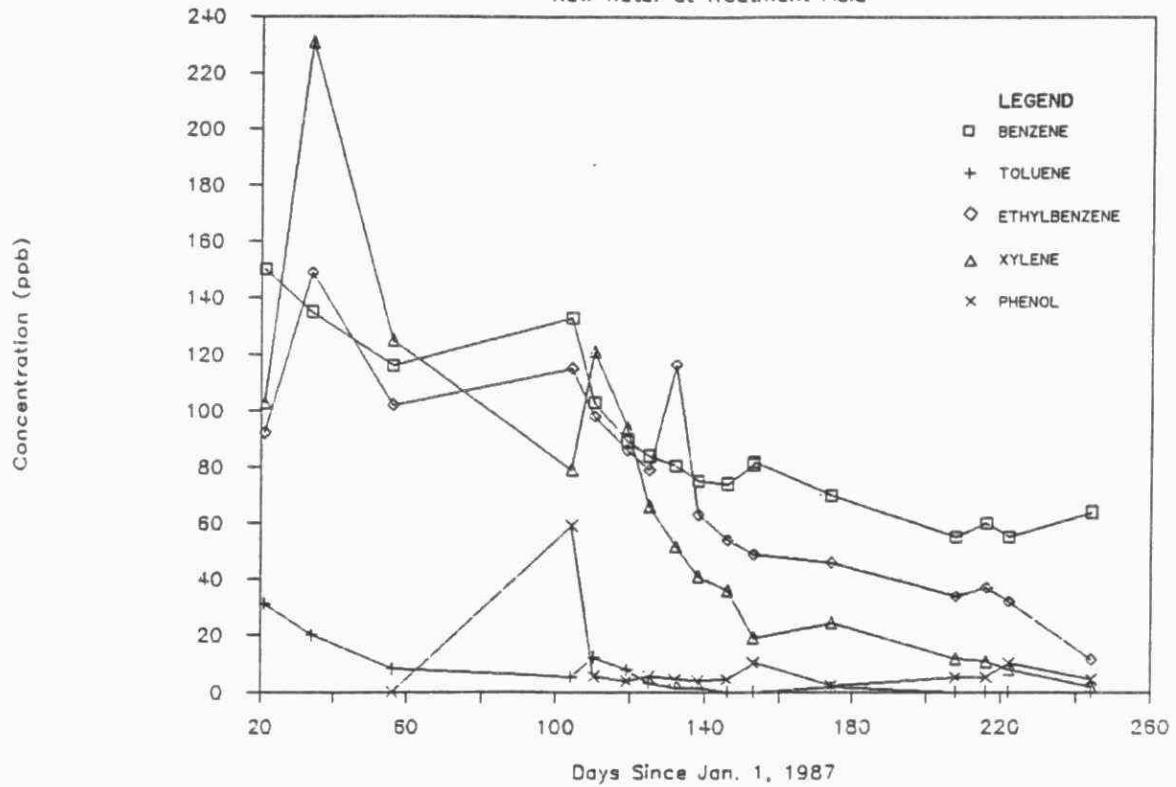


FIGURE 6

CHANGES IN CONTAMINANT CONCENTRATIONS WITH TIME, TREATMENT SITE



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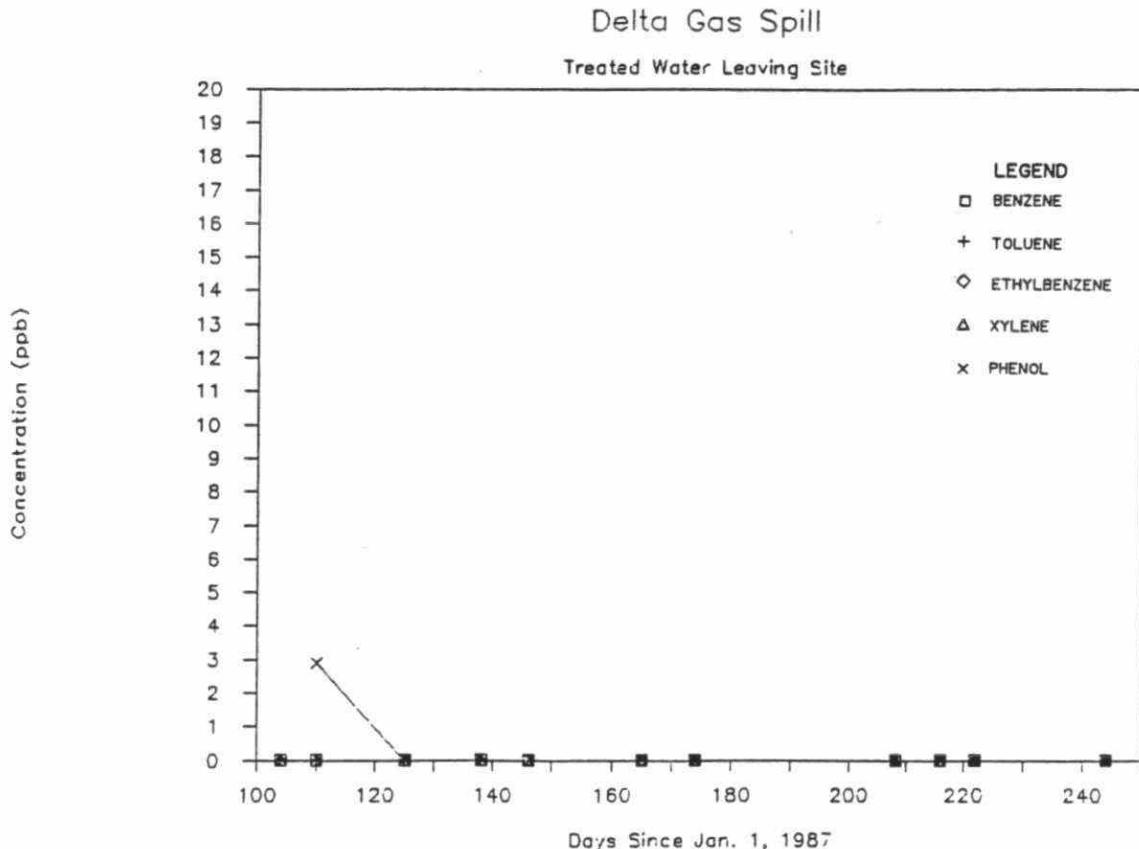
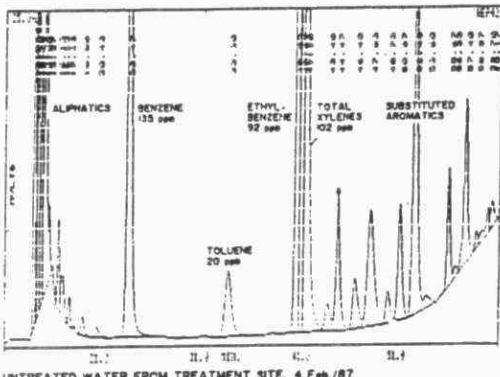


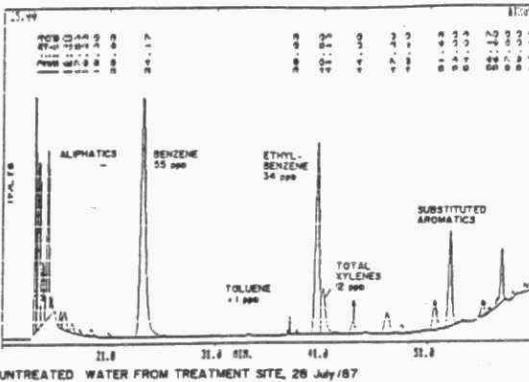
FIGURE 7
CHANGES IN CONTAMINANT CONCENTRATIONS WITH TIME



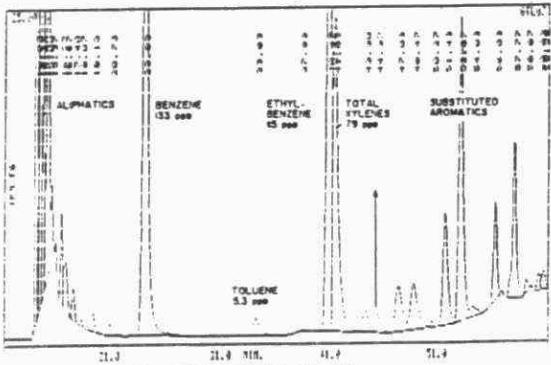
WATER AND EARTH SCIENCE ASSOCIATES LTD.



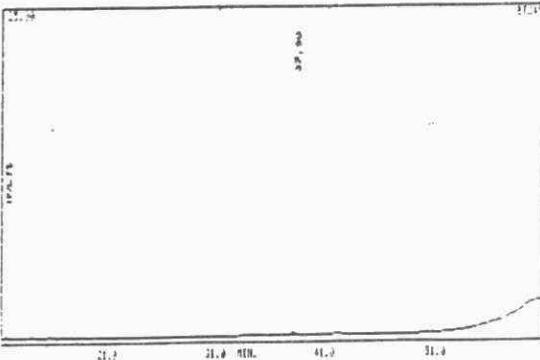
UNTREATED WATER FROM TREATMENT SITE, 4 Feb/87



UNTREATED WATER FROM TREATMENT SITE, 26 July/87



UNTREATED WATER FROM TREATMENT SITE, 15 April/87



TREATED WATER, DISCHARGE FROM TREATMENT SITE, 15 June/87

FIGURE 8
G.C. SCANS OF DELTA GROUNDWATER, TREATMENT SITE



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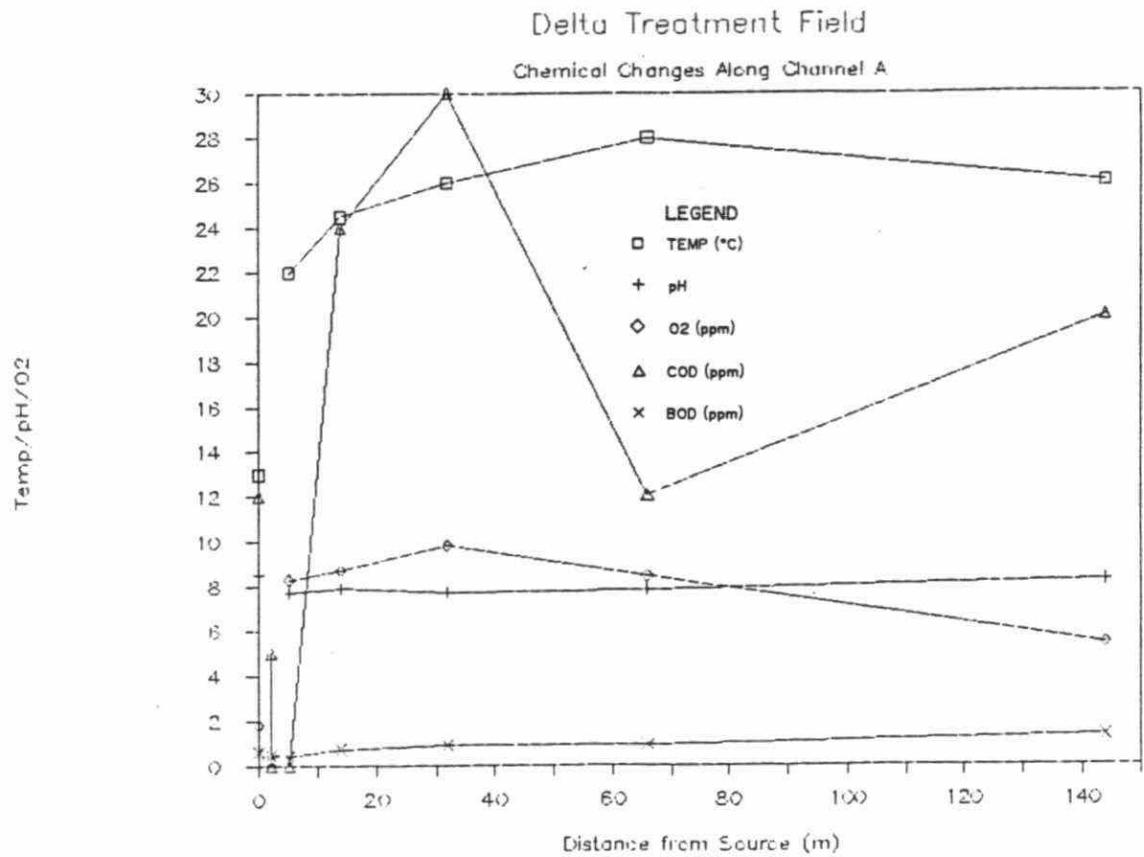


FIGURE 9
CHANGES IN CHEMICAL PARAMETERS ALONG TREATMENT CHANNEL BA



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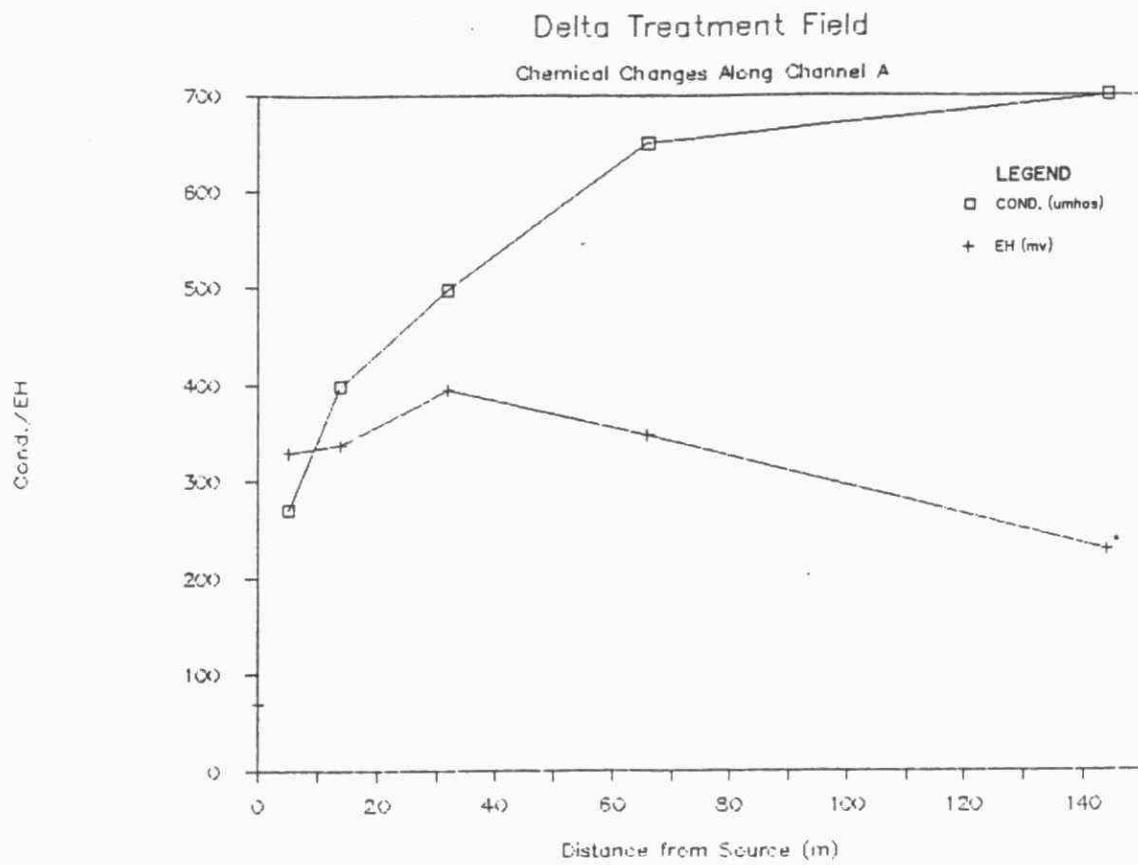


FIGURE 10
CHANGES IN CHEMICAL PARAMETERS ALONG TREATMENT CHANNEL BA



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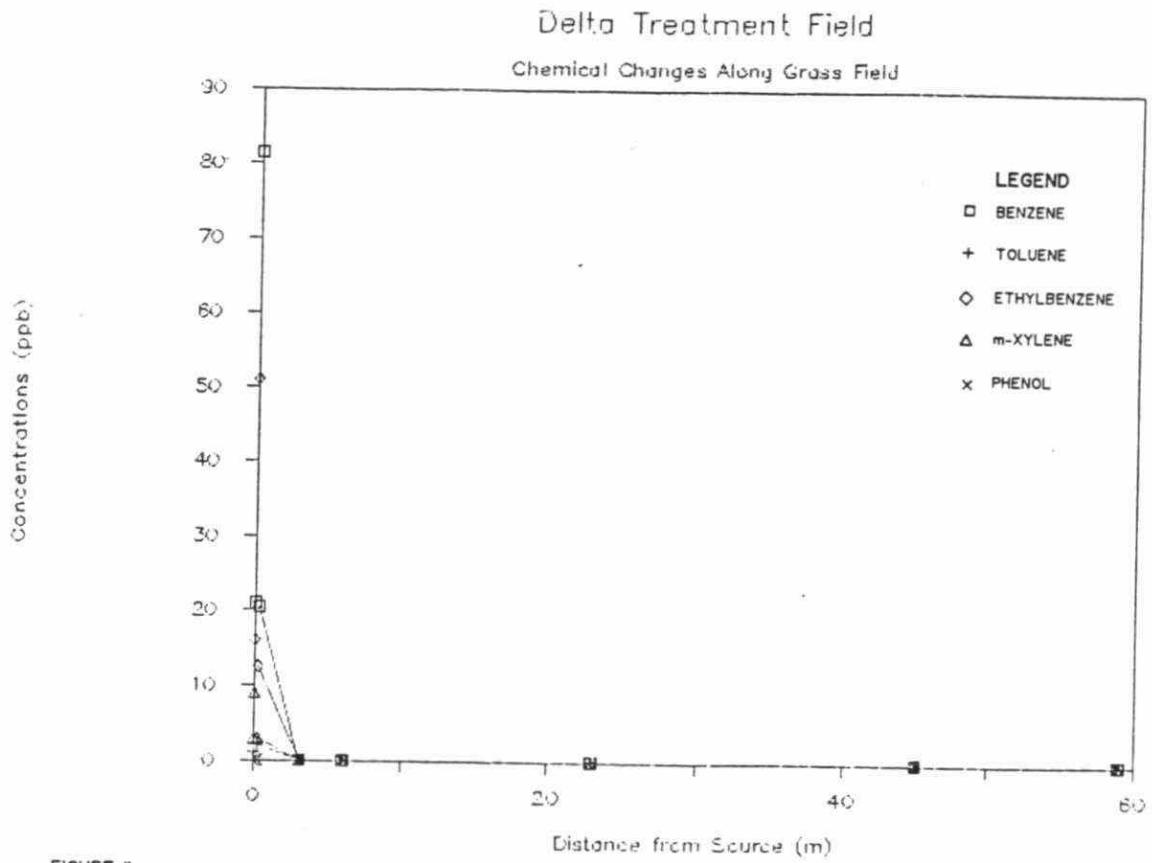


FIGURE II
CONTAMINANT CONCENTRATIONS ALONG THE GRASS TREATMENT FIELD (A)



WATER AND EARTH SCIENCE ASSOCIATES LT

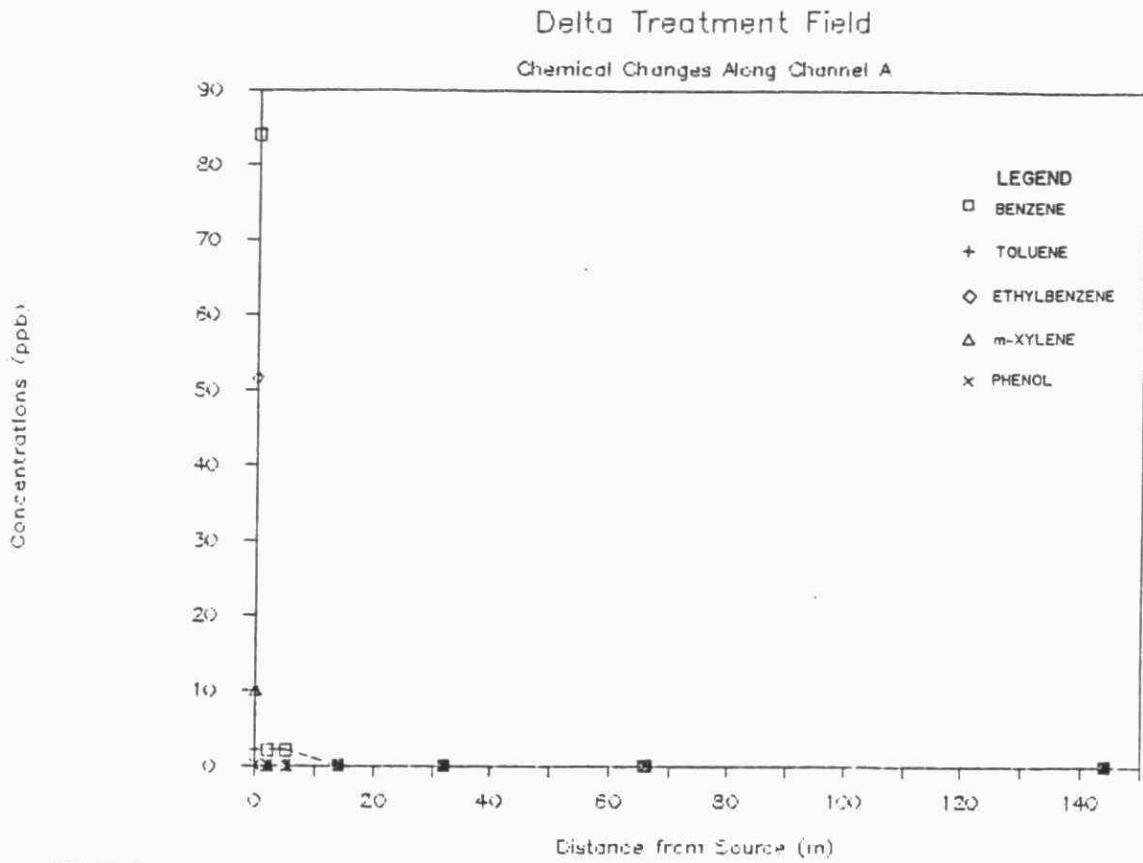


FIGURE I2
CONTAMINANT CONCENTRATIONS ALONG TREATMENT CHANNEL BA



WATER AND EARTH SCIENCE ASSOCIATES LTD.

*Ontario Ministry of the Environment
Technology Transfer Conference
Toronto, Ontario, Dec. 1987*

OPTIMAL RECOVERY OF LEACHATE UNDER SANITARY LANDFILLS

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Waterloo, Ontario, Canada N2L 3G1

ABSTRACT

Numerical simulations were performed to evaluate the efficiency of tile drain leachate collection systems beneath sanitary landfills. A two-dimensional finite element model for steady-state saturated flow was used to compute hydraulic potentials and stream functions within the flow domain. The model incorporates a specialized discretization scheme to facilitate accurate simulations at both the local and the regional scale.

Simulations were focussed on the regional scale of flow systems containing landfill drain networks. The system response was studied under several scenarios of drain system location and geometry, all based on the assumption of a tile field placed below the elevation of the natural watertable. This configuration induces flow toward the drains at all times, and thus ensures complete leachate collection. The simulation results illustrate the relationships between the design parameters and the amount of water collected from the groundwater system. The volume of water is found to be at a minimum with drains located in the recharge area of the regional system, and at a maximum with drains located in the transition zone between the recharge and discharge areas. Implications also arise with respect to drain location relative to the landfill, and to tile drain network density. Results indicate that the regional flow system must be considered to obtain an accurate prediction of tile drain performance.

INTRODUCTION

In southern Ontario, sanitary landfilling continues to be the most common method for the disposal of municipal and industrial solid wastes. Tile drain systems are often used in the landfilling operation in order to collect any leachate that escapes. Drain systems however may not always function in an optimal way; for example, leachate may bypass the collection system and contaminate an underlying aquifer, or the drain system may drain excessive amounts of water from below. Our present research program addresses these problems and investigates the relationship between leachate collection and the hydrologic and

geometric controls which govern groundwater drainage systems.

Initial work on this three-year project involved the study of drainage flow behaviour using a laboratory sand box as well as a numerical model. A summary of this previous work is provided by Farvolden et. al. (1985), Abdul et. al. (1985) and St. Arnaud et. al. (1986). A simplified flow domain was used in completing a sensitivity analysis of several design parameters. In contrast to most existing solutions to tile drainage problems, which generally apply to lined landfill drainage systems above the natural watertable, this study is directed toward induced drainage with tiles placed below the natural watertable.

The present paper investigates tile drainage on a regional scale. Landfill drain system performance is simulated in the presence of regional flow gradients and concurrently, these simulations illustrate the resulting perturbation of the regional flow system. This approach more closely approximates real-world situations compared with local-scale analyses frequently used, as some of the most restrictive boundary conditions and assumptions are eliminated.

EARLIER APPROACHES TO TILE DRAINAGE PROBLEMS

Analytical solutions to groundwater flow equations with artificial drainage are fairly extensive in the literature (see for example Wong (1977), Youngs and Al-Najim (1978), McBean et. al. (1982), Demetrasopoulos et. al. (1984) and Fougner and Byer (1984)). These earlier solutions are generally valid only for relatively simple geometry and specified boundary conditions. All require some type of impervious or leaky confining layer below the drains and above the regional watertable. The solution domain in these and most of the existing mathematical drainage problems consists of a symmetric flow field beneath the drains (Figure 1).

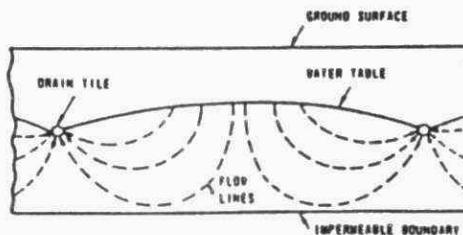


Figure 1 Simplified flow systems commonly assumed in the derivation of mathematical solutions to drainage problems.

Mathematical problems involving variable geometry, material properties and boundary conditions are generally better suited for solution using numerical methods. Several studies relating to tile drainage problems have adopted this more flexible approach.

The finite element method was used in the determination of watertable heights in drained soils by Gureghian and Youngs (1975). They applied a two-dimensional form of the steady-state flow equation to a flow domain containing a single drainage channel within a symmetric flow field. Their numerical approach provided good accuracy compared to corresponding analytical solutions and demonstrated versatility in applications to inhomogeneous problems.

Tang and Skaggs (1977), in a study of drainage flow behaviour, solve the two-dimensional saturated-unsaturated transient flow equation using the finite difference method. Although their approach is applicable to more realistic systems, they assume symmetrical flow fields in order to simplify their solution domain to one which incorporates a single drainage channel underlain by an impermeable boundary. They observed good agreement between the numerical model and laboratory test results; however, the requirement of defining field values of non-linear unsaturated soil properties led them to conclude that simpler approximate methods would be preferable for drainage design purposes.

In an analysis of coupled flow and solute transport in tile drained soils, Pickens et. al. (1979) used the finite element method to solve a similar form of the saturated-unsaturated flow equation used by Tang and Skaggs. A symmetrical section of the flow field with an impermeable base was again assumed for the solution domain. Under these conditions, with a saturated hydraulic conductivity of about 6.0×10^{-5} m/s, they observed that convergence of the flow field to steady-state could occur within only a few days. They concluded, however, that due to the fine spatial discretization required to accommodate the unsaturated zone coupled with their transient analysis, extensions to larger-scale domains would be computationally excessive.

THE FINITE ELEMENT MODEL

Steady-state groundwater flow systems in the vertical cross-sectional plane can be efficiently described by the governing equations of hydraulic potentials and stream functions (Frind and Matanga, 1985). This approach, referred to as the dual formulation, was used for both the half-cell and regional flow simulations. Basic assumptions include a steady, irrotational flow field with an incompressible fluid and a non-deforming, saturated porous medium.

The continuity equations, with the coordinate axes oriented along the principal directions of permeability, are respectively

$$\frac{\partial}{\partial x} \left(K_{xx} \frac{\partial \phi}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_{yy} \frac{\partial \phi}{\partial y} \right) = 0 \quad (1)$$

$$\frac{\partial}{\partial x} \left(\frac{1}{K_{yy}} \frac{\partial \psi}{\partial x} \right) + \frac{\partial}{\partial y} \left(\frac{1}{K_{xx}} \frac{\partial \psi}{\partial y} \right) = 0 \quad (2)$$

where ϕ is the hydraulic potential defined as $\phi(x,y) = y + p/\rho g$, with y

representing elevation head, p the pressure, ρ the fluid density and g the gravitational acceleration, and $\psi = \psi(x,y)$ is the stream function. Contours of equal stream function ψ yield streamlines which are everywhere tangent to the specific discharge vector \vec{q} . Computationally correct flownets are therefore easily generated using the dual formulation and are used extensively in this paper to provide a visual perspective of the flow fields. Accurate boundary fluxes are also determined in the solution.

Boundary conditions for equations (1) and (2) can be of the first (Dirichlet) or second (Neumann) type. In the potential equation, the first and second type boundary conditions take the form

$$\phi = \phi_0(\Gamma) \quad (3a)$$

$$g_n^\phi = q_n \quad (3b)$$

where ϕ_0 represents a given potential, for example along a specified watertable, and q_n represents a given fluid flux normal to the boundary, for example recharge into a flow basin (inward flux is defined as positive). First and second type boundary conditions for equation (2) are of the form

$$\psi(\Gamma) = \psi_0(\Gamma_0) + \int_{\Gamma_0}^{\Gamma} \vec{q}_0 \cdot \vec{n} \, d\Gamma \quad (3c)$$

$$g_n^\psi = -\frac{\partial \phi}{\partial x} \vec{r}_x - \frac{\partial \phi}{\partial y} \vec{r}_y, \quad (3d)$$

where \vec{n} is the unit outward normal vector and \vec{r}_x, \vec{r}_y are unit vectors tangential to the boundary. Equation (3c) is applied along a boundary Γ where the flux \vec{q}_0 is known. Along an impermeable boundary where $\vec{q}_0 = 0$, equation (3c) takes the form $\psi = \psi_0$ (by convention, the reference value is $\psi_0 = 0$). Equation (3d) is applied along a boundary of known potential.

Equations (1) and (2) are solved using the Galerkin finite element method using linear basis functions over triangular elements. The final set of linear equations are solved efficiently using the Cholesky algorithm for symmetric banded matrices.

In the case of a specified flux across the watertable, the watertable position is unknown beforehand and must be determined iteratively. Watertable elevations are continuously updated with computed boundary potentials until convergence is attained, which for the regional simulations presented here, consistently occurred within 3 iterations. The finite element grid is allowed to deform vertically to accommodate the moving boundary. All simulations were performed using double precision arithmetic with no significant mass balance error.

In this study, tile drains were represented in the model as boundary nodes of constant potential. This method assumes the tiles drain under gravity and possess a pressure head of zero. The hydraulic potential of the drains is therefore equivalent to drain elevation. This method of drain representation was chosen to allow drain flux to vary according to the imposed hydrologic conditions. The fluid flux at the drains is here computed, after solving for potentials, from the partitioned form of the finite element matrix equations (Frind and Matanga, 1985). Additional boundary conditions applicable to drains are presented and compared by Fipps et. al. (1986). They concluded that a constant potential applied at a drain will give accurate results, provided that near the drains the spatial resolution is sufficiently fine.

PREVIOUS APPLICATION OF THE MODEL:

THE HALF-CELL APPROACH

The half-cell approach is based on the idealized flow field beneath a tile drain network illustrated in Figure 2a. Assuming symmetry about the drains, and neglecting regional flow gradients, a typical drain flow system can be represented by the half-cell section shown in Figure 2b. The first phase of this modelling study used a flow system domain of this type (St. Arnaud et. al., 1986). The half-cell is contained between two vertical symmetry boundaries with a high permeability layer at depth represented as a constant potential boundary. A uniform recharge function (R) is applied over the watertable. The drain is represented by a constant potential boundary node, and the watertable position is iteratively determined while deforming the grid. A sample grid configuration following watertable convergence is shown in Figure 2c.

The dual formulation was used to solve for steady-state potentials and stream functions, the contours of which produce flownets such as illustrated in Figure 2d. Computed boundary fluxes were used to quantify drain efficiency under variable recharge, hydraulic conductivity, geometry and vertical flow gradients.

Results from simulations using this system indicated that leachate collection is most efficient with gradients inducing upward flow and efficiency increased as tile spacing decreased. Conditions of optimal recovery were, however, sensitive to variations in all parameters examined and general guidelines relevant to field situations were deemed difficult to obtain. Preliminary regional flow simulations suggested that the assumptions of the half-cell system are satisfied with vertically downwards regional flow, but not with horizontal regional flow.

THE REGIONAL SCALE APPROACH

Application of the numerical model to regional scale drainage simulations required the definition of realistic flow fields which would include recharge and discharge flow conditions and impose few artificial constraints on the problem. These criteria were satisfied with flow systems derived from a Hubbert-type cross section (Figure 3a). This regional flow domain has an impermeable

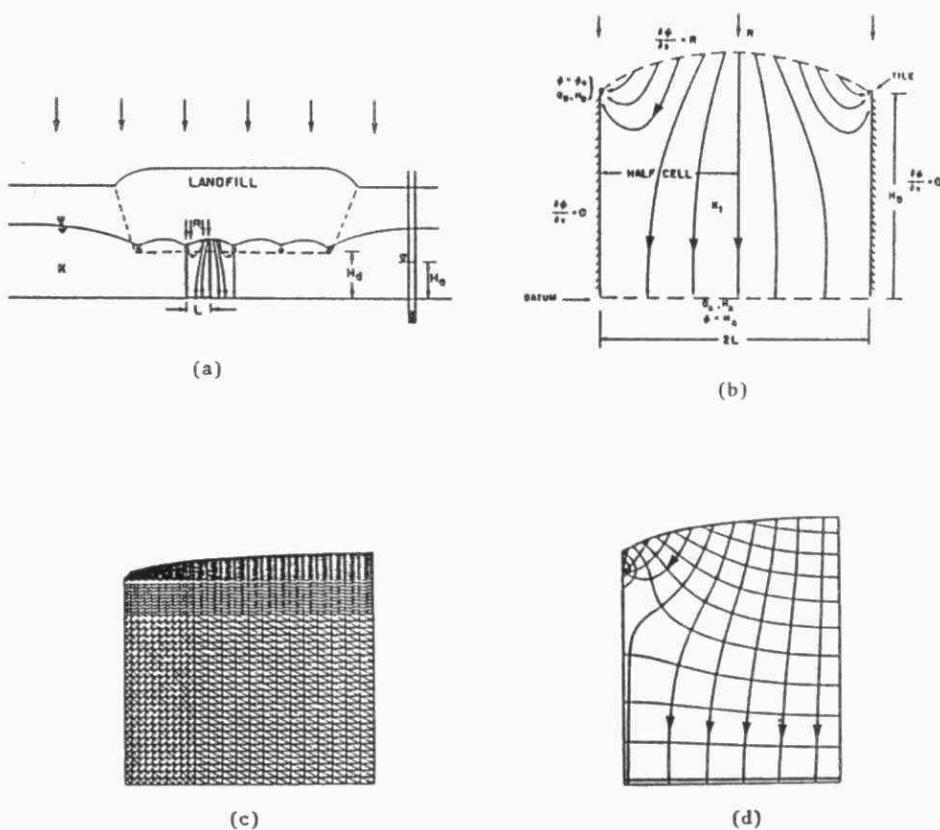


Figure 2 Application of the numerical model using the half-cell approach: (a) idealized tile drain flow fields beneath a landfill, (b) boundary conditions of the half-cell, (c) grid configuration, (d) sample flownet.

boundary along the base with vertical symmetry boundaries representing basin flow divides. A uniform hydraulic conductivity of $K_{xx} = K_{yy} = 10^{-5}$ m/s was assumed. The flow system is driven by a half-wavelength cosine function defining the watertable elevation. The Darcy flux which sustains this flow is plotted above the watertable in Figure 3a.

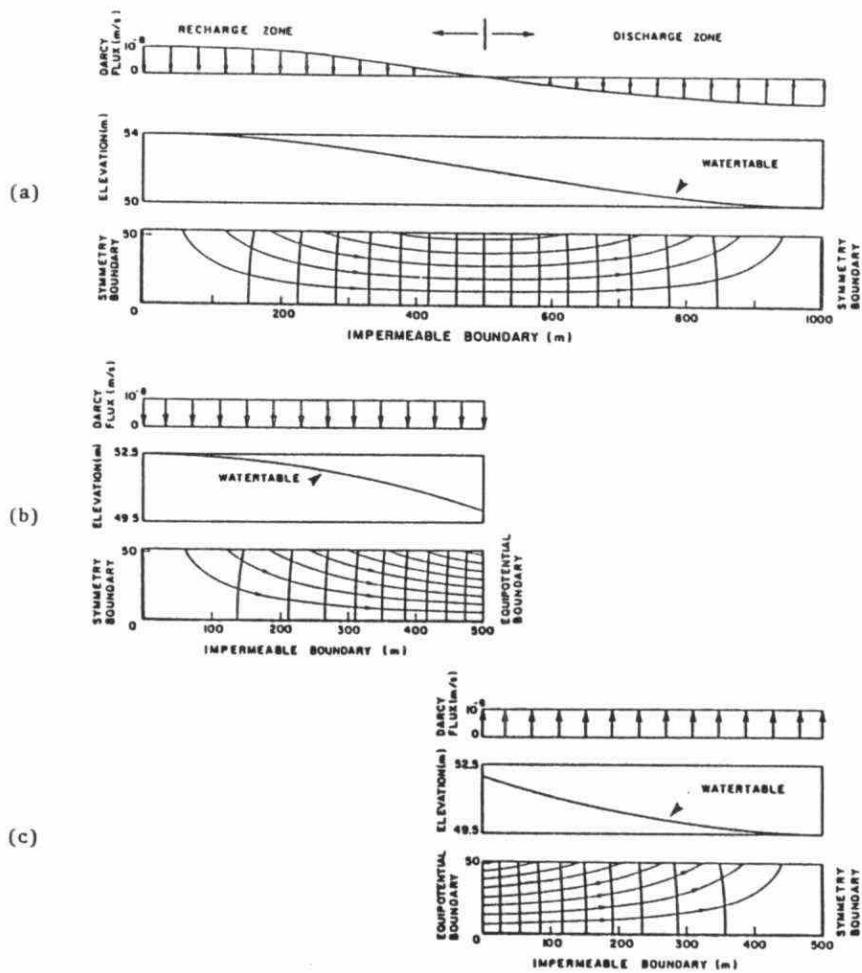


Figure 3 Definition of regional flow systems: (a) Hubbert flow field, (b) idealized recharge domain, (c) idealized discharge domain.

For the purpose of studying the performance of drains located in either the recharge or discharge zone of a regional flow system, the system of Figure 3a was simplified by division into two sections (Figures 3b and 3c). The vertical equipotential existing at the centreline of the regional section was applied as a constraint on the new boundaries where the separation was made. The recharge and discharge functions were also simplified by assuming uniform distributions as shown. The equilibrium watertable positions (iterated to convergence) assume a parabolic form. The two subsystems now represent recharge and discharge zones of the regional flow system.

Figure 4 defines the 2D domain including its boundaries. In the recharge flow domain, Γ_1 represents a symmetry flow divide across which there is no flow, while Γ_4 takes the form of a Dirichlet equipotential boundary. These conditions are reversed for the discharge flow domain. Following the procedure adopted for the half-cell simulations, the drain boundary Γ_2 is assigned a fixed potential, equivalent to the desired drain elevation. The watertable boundary Γ_3 is a Neumann type with a given Darcy flux distribution. The lower boundary Γ_5 is impermeable.

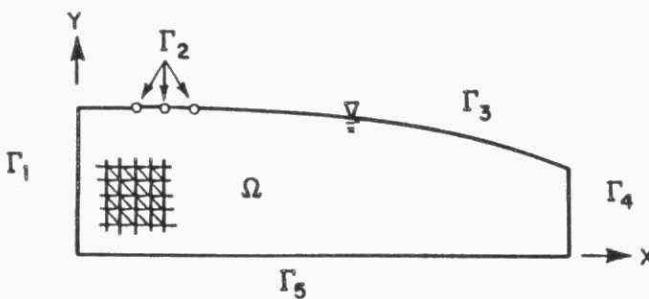


Figure 4 Boundaries of regional subsystems.

The numerical modelling of tile drain systems within a regional flow field presented problems of simulation scale and spatial discretization. Although the entire domain must be covered by the finite element grid, the areas nearest the drains require a much finer resolution to account for drain scale geometry and to maintain accuracy in areas of contorted flow fields expected near the drains. A hypothetical setting of a landfill (Figure 5a) illustrates the scales involved.

The approach adopted to accommodate the regional and local drain scales involved the use of a specialized grid generator to create areas of higher element density surrounding the drain nodes. A sample grid which would be used to discretize the domain of Figure 5a is shown in Figure 5b, and details of the innermost grid are shown in Figure 5c. The position of the fine grid containing the drains can be changed within the flow system to allow the simulation of drain response under varying flow gradients.

SIMULATIONS OF REGIONAL SCALE TILE DRAINAGE

Regional scale simulation results are presented in the form of flownets plotted at two scales, the regional scale and the magnified local scale in the vicinity of the drains. These local scale flownets correspond to the zone of high grid density around the drains, as shown in Figure 5c. Regional scale flownets were plotted with a vertical exaggeration of 2 while the local scale flownets have no vertical exaggeration. Contour intervals of potentials and stream functions are indicated in the figures.

The watertable, forming the upper boundary of each flow domain, is plotted above each regional flownet. The background watertable elevation, conforming to the natural flow field without drains, is also included as a basis for comparison.

The simulations included here relate important design variables to drain system performance and flow field response. Among several design aspects studied, those considered most significant were: (a) landfill drain network location with respect to the regional flow system; (b) drain depth below the natural background watertable; and (c) the number of tiles and their spatial distribution within the tile field.

Flow system behaviour as a function of drain network location is illustrated in Figures 6, 7 and 8. Two locations are considered in each of the recharge and discharge flow systems and one in the centre of the full regional flow system. These simulations cover the extremes of mean vertical and horizontal flow gradients as well as intermediate transition zones. In each case, the drain system consists of 21 tiles, represented by constant-head nodes, distributed uniformly in the horizontal over a length of 20.0 metres, and placed at a drain depth of 0.7 m below the natural watertable. References to drain network location are understood to be with respect to the centre point of the drain array.

Figures 6a and 6b show the flownets for the recharge flow system with the drain network located at a distance of 65.0 and 225.0 metres, respectively, from the left (upstream) flow divide boundary. In the location closest to the divide (Figure 6a), the presence of the drains creates a small local flow system that drains an area of about 50 m^2 per unit width of section, discharging about $0.04 \text{ m}^2/\text{day}$. Details of the local system are shown in the enlarged figure. The tiles draw discharge from both sides of the drain field. The remainder of the regional flow system is also affected because the horizontal gradients, and hence the flow in the section, are reduced.

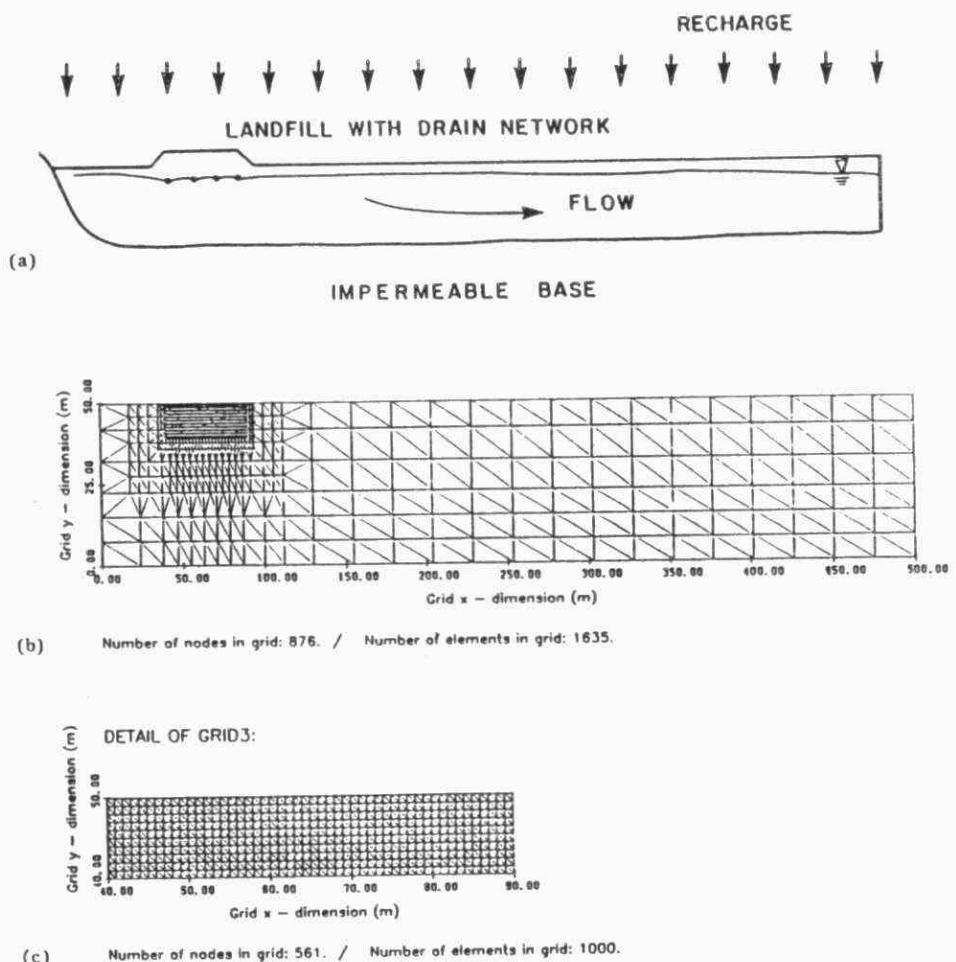


Figure 5 Regional scale system discretization: (a) hypothetical landfill setting, (b) finite element grid discretization, (c) fine grid detail.

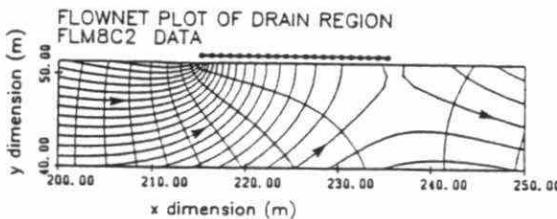
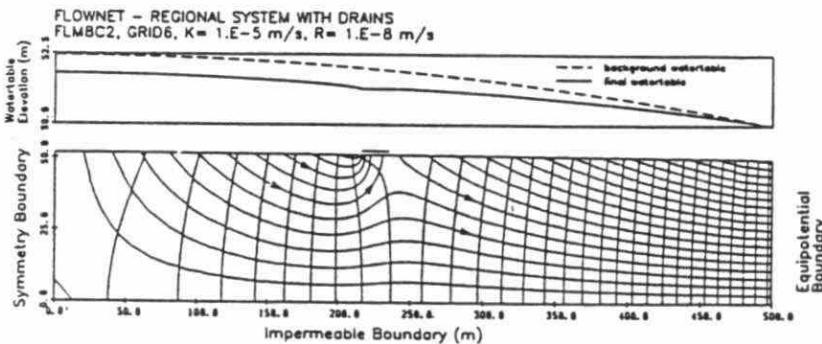
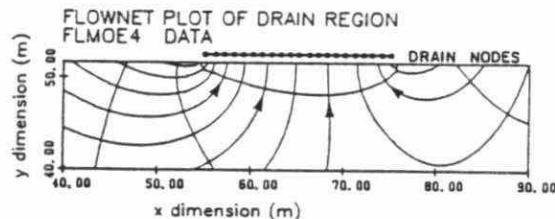
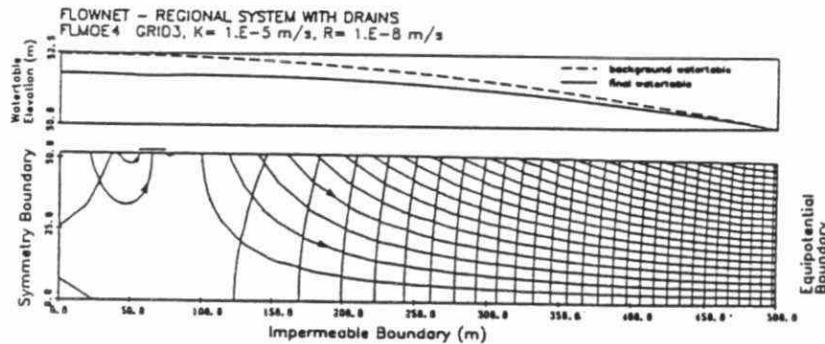


Figure 6 Regional flow drainage simulations - recharge domain; (a) drain array 65.0 m from left boundary, (b) drain array 225.0 m from left boundary. (regional flownet: $\Delta\phi = .06$ m, $\Delta\psi = 2. \times 10^{-7}$ m²/s; local flownet: $\Delta\phi = .015$ m, $\Delta\psi = 5. \times 10^{-8}$ m²/s)

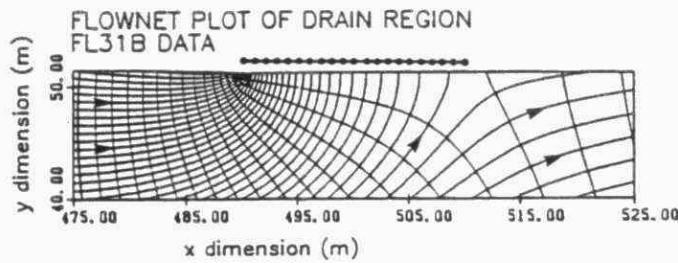
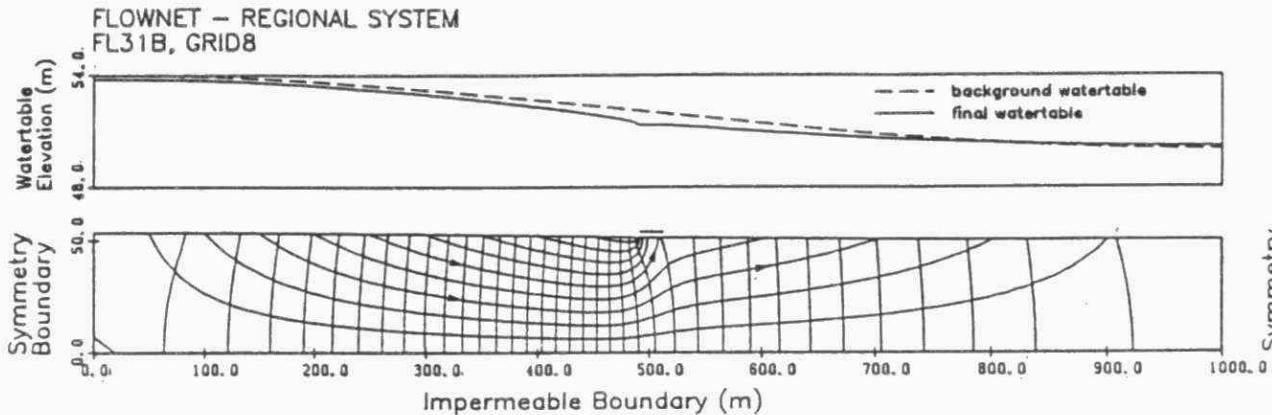


Figure 7 Regional flow drainage simulation within Hubbert flow field.
(regional flownet: $\Delta\phi = .1$ m, $\Delta\psi = 5 \times 10^{-7}$ m²/s; local flownet:
 $\Delta\phi = .018$ m, $\Delta\psi = 8 \times 10^{-8}$ m²/s)

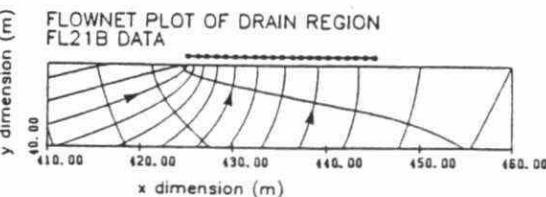
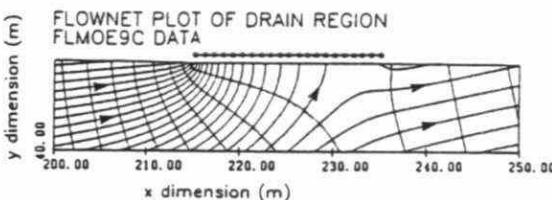
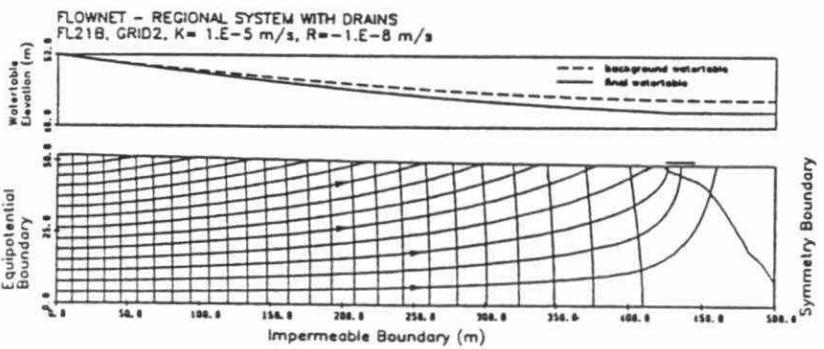
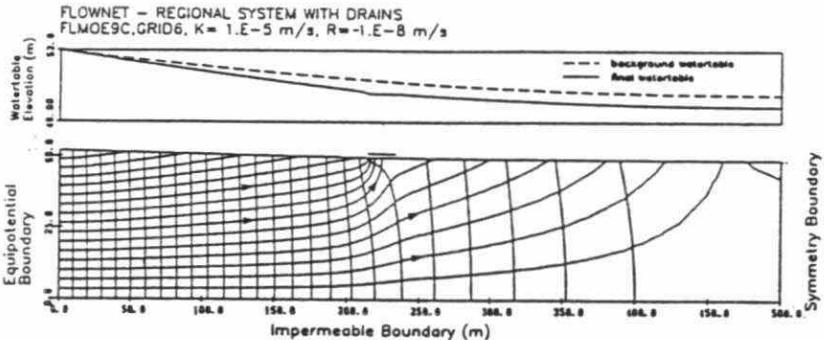


Figure 8 Regional flow drainage simulations - discharge domain; (a) drain array 225.0 m from left boundary, (b) drain array 435.0 m from left boundary. (regional flownet: $\Delta\phi = .12$ m, $\Delta\psi = 4. \times 10^{-7}$ m²/s; local flownet: $\Delta\phi = .03$ m, $\Delta\psi = 1. \times 10^{-7}$ m²/s)

As the drain system is moved to a point 225.0 m downgradient from the divide (Figure 6b), the interception of regional flow by the drains increases. The flownet shows that now an area of about 125 m^2 per unit width of section is drained, with a discharge of $0.07 \text{ m}^2/\text{day}$. Due to the strong horizontal gradients that exist in the area of the drains, all discharge now originates upgradient from the drains. The tiles near the upgradient side carry a much greater load than those near the downgradient side of the drain field. The regional flow field is strongly affected by the presence of the drain field in this location.

In Figure 7, the drains are placed in the centre of the complete regional flow system at a depth of 0.7 m below the background watertable. The boundary flux at the watertable consists of a uniform recharge of $8.6 \times 10^{-4} \text{ m/day}$ in the left half of the system, and initially, an equal uniform discharge in the right half of the system.

Tile drainage simulations within this regional flow field required an additional iterative cycle to determine an equilibrium watertable boundary discharge function. This discharge function, assuming a fixed recharge distribution independent of drainage, must be allowed to equilibrate to a level dependent on the drain discharge while satisfying the mass balance constraint on the system. A convergence criteria is obtained through requiring all drain nodes to be discharging. Initially, to satisfy mass balance, some proportion of the drains will be recharging into the system. This is an invalid condition with a saturated flow model since physically this represents a condition where the equilibrium watertable position is below the level of the drains. A solution is obtained then, by successively decrementing the discharge function over the downstream half of the system until all drains at the centre of the system are discharging.

This procedure was followed for the simulation represented in Figure 7 in which all drains were discharging when the downstream discharge function reached a value of $4.3 \times 10^{-4} \text{ m/day}$. The drain network in this system discharges at the rate of approximately $0.17 \text{ m}^2/\text{day}$ and drains a surface area of approximately 250 m^2 per unit width of section. In this central location, horizontal gradients are at a maximum, and as a consequence, the disturbance to the regional flow system is at a maximum, with the drains intercepting the maximum amount of flow from the regional system. Discharge in the tiles is most heavily concentrated in the upstream portion of the tile field.

In the discharge subdomain, the drain network is located at 225.0 and 435.0 metres respectively from the left equipotential boundary with the drains 0.7 m below the background watertable (Figures 8a, 8b). Horizontal flow gradients now decrease toward the right and accordingly, drain discharge decreases. Drain discharge magnitudes are approximately $0.14 \text{ m}^2/\text{day}$ and $0.07 \text{ m}^2/\text{day}$ for the two locations respectively, approximately double the corresponding values for the recharge zone, but less than the value for the centre of the regional system. The surface area that is drained by the tile system in each case is located in the recharge area of the regional system, which is exterior to the domain of the downstream subsystem. Although the flownets for these two

cases do not show much distortion compared with the flownet for the natural system, the presence of the tile system does cause an increase of the gradient upstream and a general lowering of the watertable downstream of the drains. Within the tile fields, discharge is again concentrated more heavily in the upgradient part.

The above scenarios are all based on a constant drain depth of 0.7 metres below the background watertable. To illustrate the effect of drain depth, the depth of the two recharge area tile fields (Figures 6a and 6b) was increased to 1.1 m with respect to the background watertable. The resulting flow fields are shown in Figures 9a and 9b.

The effect of the increased drain depth is reflected by an increase in drain discharge to $0.08 \text{ m}^2/\text{day}$ and $0.11 \text{ m}^2/\text{day}$ for the two locations respectively. The surface area drained also increases to approximately 110 m^2 and 190 m^2 per unit width of section, respectively. The detailed flownet of Figure 9a reveals that under these higher vertical flow gradients, nearly symmetric flow occurs toward the drain field, drawing almost equal amounts of surface recharge from both sides of the network. The flow gradients beneath the tiles of Figure 9b have also increased to the point where a small component of drainage is derived from the downgradient side of the drains.

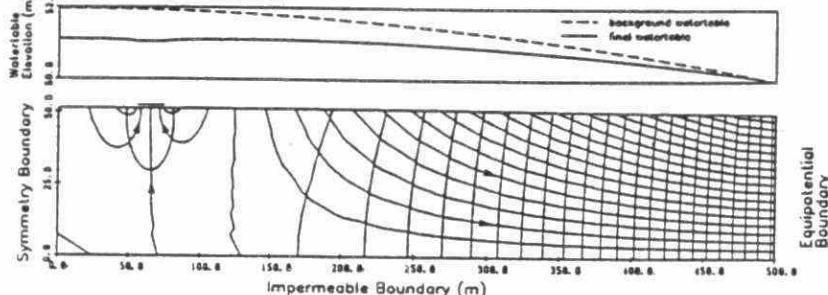
The tile field located near the middle of the recharge area (Figure 6b) was used to investigate the effect of the drain density and spacing. For this purpose, the number of drains was reduced from 21 to 6, keeping the drain field width and depth the same. The free watertable between the tiles is represented by a number of flux boundary nodes, with a recharge flux equal to the background flux over the entire section ($8.6 \times 10^{-4} \text{ m/day}$). The resulting flow field, shown in Figure 10a, is almost identical to that with 21 drains (Figure 6b). Only some minor local flow perturbations occur near the tiles. In addition, the total drain discharge and the surface area drained remain very nearly the same.

Finally, the tile field was further simplified to a single drain (Figure 10b). This causes the flow field near the drain to become nearly radially symmetric. The regional flow system, however, compared with the 21-tile drain field, is not changed significantly, and the total discharge and surface area drained again remain essentially the same.

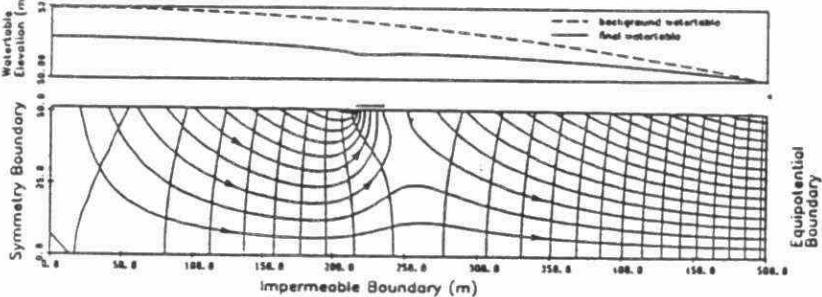
CONCLUSIONS

Several implications relevant to landfill tile drain design arise as a result of the model simulations. Under all conditions, tile drain fields placed below the natural watertable influence the natural flow system in such a way that flow will always be toward the drains. Thus no leachate can reach the groundwater system, but a certain amount of groundwater is always collected from outside the landfill area. This condition, which is independent of whether or not the landfill is capped, will hold as long as the natural watertable in the vicinity of the drains remains above the tile elevation.

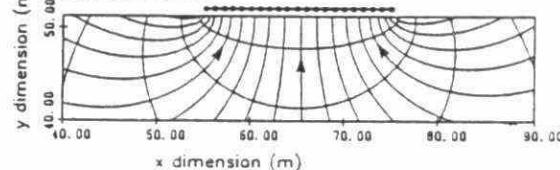
FLOWNET - REGIONAL SYSTEM WITH DRAINS
FLM8C, GRID3, K= 1.E-5 m/s, R= 1.E-8 m/s



FLOWNET - REGIONAL SYSTEM WITH DRAINS
FLM8C, GRID6, K= 1.E-5 m/s, R= 1.E-8 m/s



FLOWNET PLOT OF DRAIN REGION
FLM8C DATA



FLOWNET PLOT OF DRAIN REGION
FLM8C DATA

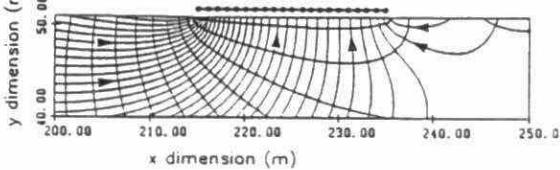


Figure 9 Regional flow drainage simulations - effect of drain elevation at 1.1 m below natural watertable; (a) drain array 65.0 m from left boundary, (b) drain array 225.0 m from left boundary.

(regional flownet: $\Delta\phi = .06$ m, $\Delta\psi = 2. \times 10^{-7}$ m²/s; local flownet: $\Delta\phi = .015$ m, $\Delta\psi = 5. \times 10^{-8}$ m²/s)

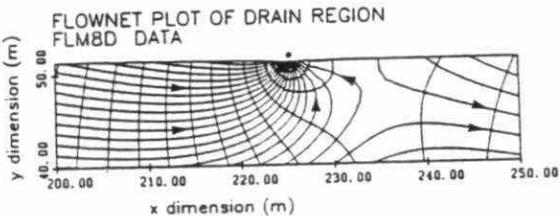
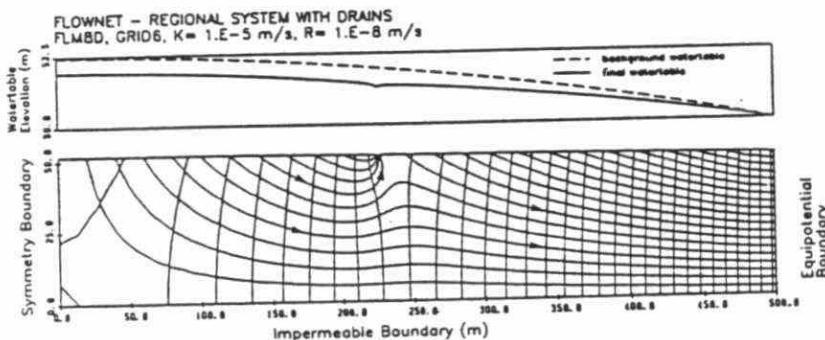
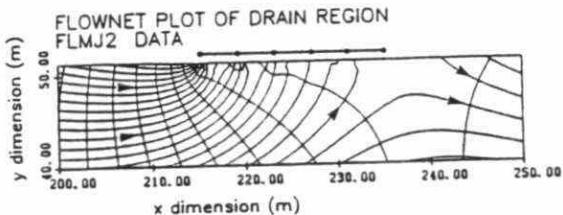
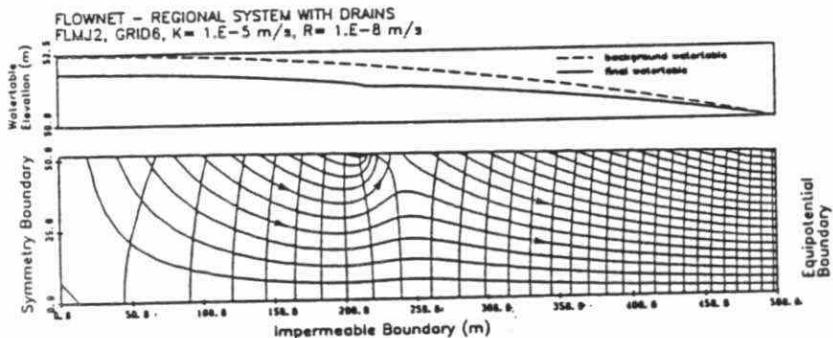


Figure 10 Regional flow drainage simulations - effect of drain spacing;
 (a) array of 6 drains over 20.0 m, (b) array of single drain over 1.0 m.
 (regional flownet: $\Delta\phi = .06 \text{ m}$, $\Delta\psi = 2. \times 10^{-7} \text{ m}^2/\text{s}$; local flownet:
 $\Delta\phi = .015 \text{ m}$, $\Delta\psi = 5. \times 10^{-8} \text{ m}^2/\text{s}$)

This behaviour is in contrast to that of the half-cell system which neglects regional effects and thus shows downward flow, some of which may bypass the drains. Thus the concept of collection efficiency, defined within the context of the local half-cell system as the amount collected relative to the amount recharged, loses its meaning within the context of the regional system study. Under the conditions of regional flow, with drains positioned below the natural watertable at all times, the system that collects the least amount of groundwater will be optimal.

The amount of groundwater collected is related to the horizontal groundwater gradient in the area of the tile field. With the tile field placed within a natural recharge area, the area influenced, and the amount collected, is relatively small. As the drain field is moved downstream from the recharge area, the area of influence of the drain field, and the amount collected from the flow system, increases. A maximum is reached when the drains are located in the transition zone between the recharge and discharge areas where horizontal gradients are largest. Further moving the drain field into the discharge area of the regional flow system again reduces the area of influence and the volume of water collected from the system. The volume collected by drains in the regional discharge zone will, however, be greater than that collected at a corresponding location in the regional recharge zone.

Tile drain networks within regional recharge flow systems generally collect a greater proportion of fluid from the surface area upgradient of the drains. This proportion varies with drain position and suggests that optimum collection efficiency may be achieved with drain arrays placed somewhat downgradient from the landfill. Further, the distribution of outflow at the tile fields varies significantly within the drain array depending on location and elevation. Generally, the tiles located at the edge of the tile field on the upgradient side carry the greatest load.

The effect of spacing and number of tiles in the tile field generally extends to the flow field in the immediate vicinity of the drains only, but not to the regional flownet. The total drain discharge is also unaffected. Thus a single drain in a regional system can theoretically collect the same amount as a large number of closely spaced drains.

In summary, the results suggest that the optimal location for a landfill with respect to drain design is in the recharge zone of a regional flow system, provided the tile field is placed such that the tile elevation remains below the elevation of the natural watertable at all times. For landfills located elsewhere within a regional flow system, drains installed downgradient of the landfill area may be advantageous. Under these conditions, a small number of drains may be as effective as a widely dispersed tile field. This concept however requires further study, particularly with respect to seasonal effects.

Further generic regional simulations will be helpful in developing quantitative guidelines for tile drain system design in the case of relatively simple geologic settings. More complex real-world situations however will be investigated more effectively by site-specific simulation studies.

ACKNOWLEDGEMENTS

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EFFECTS OF INCREASING AMOUNTS OF NON-POLAR ORGANIC LIQUIDS
IN DOMESTIC WASTE LEACHATE ON THE HYDRAULIC CONDUCTIVITY
OF CLAY LINERS IN SOUTHWESTERN ONTARIO

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ABSTRACT

Laboratory studies have shown that the hydraulic conductivity, k , of a clay liner can be greatly increased by some concentrated organic solvents. Water-soluble organic liquids such as acetone, alcohols and dioxane are capable of displacing the water in the pores, collapsing the double layers around the clay particles and rendering a clayey barrier as pervious as sand.

Hydraulic conductivity tests have been performed on water-compacted clays permeated with domestic waste leachate spiked with increasing amounts of ethanol ($\epsilon = 32$) and dioxane ($\epsilon = 2$), respectively. The results show that hydrocarbon contents greater than 70% are required to produce significant increases in k even at zero confining pressures. Within this range of organic contents, increased permeant viscosity results in significant (up to 70%) decreases in k . For concentrated organic liquids the application of vertical confining pressures suppresses a large portion of the increases in k as a result of vertical consolidation and K_0 effects that reduce side wall leakage.

Hydraulic conductivity tests are also presented for dry clays mixed and permeated with aqueous solutions of hydrocarbons. This fundamental study illustrates the combined effects of permeant viscosity, double layer collapse and fabric on k . Pore size distributions obtained by mercury intrusion porosimetry are presented as an aid in interpreting variations in soil fabric.

Extensive studies are continuing to establish the magnitude of the in situ stresses required to minimize liquid hydrocarbon related damage.

INTRODUCTION

This paper reports on the results of our second year of study on the effects of water-soluble organic liquids in domestic waste leachate on the hydraulic conductivity of brown (weathered) clayey soils from southern Ontario. This paper should be read in association with our two previous reports presented in the 6th and 7th Technology Transfer Conferences (Quigley and Fernandez, 1985 and Quigley, Fernandez and Yanful, 1986).

The effect of organic solvents on the integrity of clay liners has been a subject addressed in several studies published during recent years and it has come to be generally accepted that concentrated organic liquids, less polar than water, are capable of producing dramatic increases in the hydraulic conductivity, k , of clays. In a very recent review on the topic, Mitchell and Madsen (1987) demonstrated that k test results are dependent on the testing techniques adopted (flexible wall vs rigid wall vs consolidation permeameter) and much understanding of both the chemistry and the test techniques is required to select test procedures which best represent the field conditions. The authors also noted that little work has been reported using permeants composed of aqueous solutions of organics or mixtures of organic solvents, even though such mixtures are likely to be found in field situations.

In the present study, ethanol (ethyl alcohol) and p-dioxane (diethylene ether) have been used as the organic liquids since they are completely soluble in water and aqueous domestic leachate and since they represent solvents of intermediate and very low dielectric constant respectively. Furthermore, previous work by the authors (Fernandez and Quigley, 1985) identified the solubility of a permeant in water as a significant factor required to produce increases in k . The viscosity and dielectric constant of aqueous solutions of the two selected organics are described in the next section as they play major roles in the interpretation of the test results. The hydraulic conductivity test results are presented in two separate sections corresponding to two different methods of sample preparation and testing. The first section describes fundamental studies carried out on dry clays mixed and permeated with aqueous solutions of hydrocarbons and illustrates the

interrelated roles of double layer collapse, permeant viscosity and compaction-induced fabric on the measured values of k . The second section presents two series of hydraulic conductivity tests performed on water-compacted clay samples permeated with domestic waste leachate containing a complete range of ethanol and dioxane.

VISCOSITY AND DIELECTRIC CONSTANT OF PERMEANTS

The permeants were prepared by mixing leachate with increasing amounts of ethanol or dioxane. The leachate was obtained from the collection manhole at the Westminster Sanitary Landfill, City of London, Ontario, and is considered to be representative of raw domestic waste leachate. The ethanol used was commercial grade (95%) and was purchased from Commercial Alcohols Limited (Montreal, Varennes, Toronto). The reagent grade dioxane used had an assay value of 100.0% and was manufactured by J.T. Baker Chemical Co. (Phillipsburg, NJ 08865).

Kinematic viscosities, v , of the permeants were measured using a Cannon-Fenske routine viscometer and are shown on Figure 1. The values are presented as the ratio of the kinematic viscosity of the mixture to that of pure water which has a viscosity of unity at 20°C. Corresponding curves for water/hydrocarbon mixtures are also presented. The density and viscosity values of the liquid mixtures are also presented in Tables I to IV. In all cases the viscosity of the solutions increases with increasing content of organics as a result of enhanced structural order in the liquid mixtures. At concentrations of ~ 40% ethanol and ~ 60% dioxane, the viscosity of the mixtures reaches values triple and double that of water, respectively. These large variations in permeant viscosity have a significant effect on the hydraulic conductivity results discussed in the following sections. It should be noted that other water-soluble solvents such as acetone, methanol, etc. exhibit similar patterns of viscosity (Flick, 1985).

The dielectric constants of aqueous solutions of ethanol and dioxane are presented on Figure 2 and in Table V. The values were calculated from the capacitance of a specially designed capacitor filled with the liquid mixtures. The results show a steady trend of decreasing

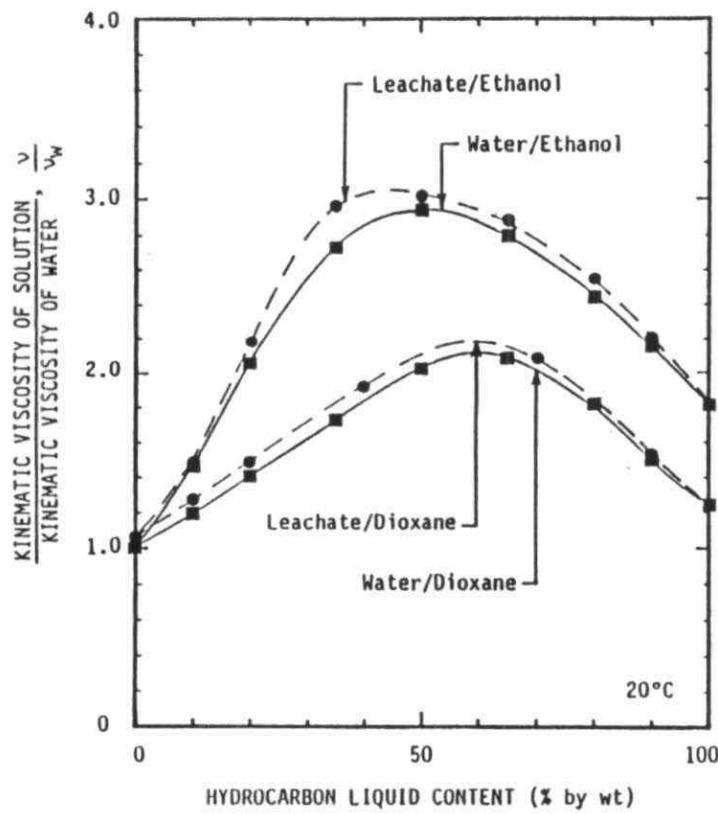


FIGURE 1. RELATIVE VISCOSITY OF SOLUTIONS
CONTAINING HYDROCARBON LIQUIDS
[Note: All values relative to pure water]
[Directly from Fernandez and Quigley, 1987]

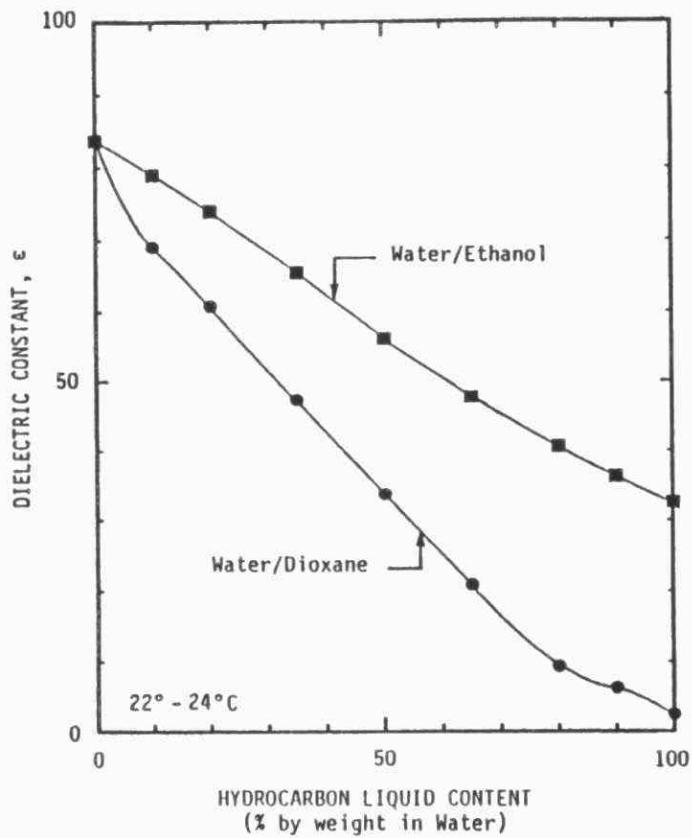


FIGURE 2. DIELECTRIC CONSTANT OF SOLUTIONS
CONTAINING HYDROCARBON LIQUIDS
[Directly from Fernandez and Quigley, 1987]

dielectric constant from ~ 84 for pure water to ~ 2.3 for pure dioxane and ~ 32 for concentrated ethanol.

HYDRAULIC CONDUCTIVITY

The hydraulic conductivity tests were carried out using a constant flow rate, rigid wall permeameter with capability for application of effective stresses, σ_v' , from 0 to 350 kPa (Fernandez and Quigley, 1985). The clay samples tested were obtained from the oxidized surface crust of a clay deposit near Sarnia, Ontario. The results are presented in terms of both hydraulic conductivity, k (cm/s) and intrinsic permeability, K (cm^2). The two are related as follows:

$$K = \frac{k v}{g} = \frac{k \mu}{g \rho}$$

where v is the kinematic viscosity of the permeant (cm^2/s = Stoke); ρ is the permeant density (g/cm^3); μ is the absolute or dynamic viscosity of the permeant ($\mu = v \cdot \rho$); and g is the gravitational constant = $981 \text{ cm}/\text{s}^2$. The intrinsic permeability, K , excludes the effect of the permeant molecular friction (viscosity) and gravity (permeant density) on flow.

HYDRAULIC CONDUCTIVITY TESTS ON CLAY SAMPLES MOULDED AND PERMEATED WITH AQUEOUS SOLUTIONS OF ORGANICS

Hydraulic conductivity studies on water-compacted clay samples often require long testing periods and/or the use of high hydraulic gradients to obtain equilibrium values of k . Dried clay samples, mixed and permeated with the test liquids, on the other hand, reach chemical equilibrium in a shorter time period which reduces permeation time considerably. For this reason, this type of testing is occasionally suggested as an option for studies of waste/clay liner compatibility. Furthermore, previous use of this technique has yielded useful information on the behaviour of clay/organic liquid systems (Michaels

and Lin, 1954; Mesri and Olson, 1971; Fernandez and Quigley, 1985). However, it must be kept in mind that since the soils are thoroughly exposed to the permeant, maximum permeant influence on the soil fabric (normally flocculation) takes place during sample preparation, which does not resemble the field situation where clay liners are normally compacted with fresh water.

The results of a series of tests on clay samples moulded and permeated with aqueous solutions containing increasing amounts of hydrocarbons are presented on Figures 3 to 6.

Figure 3a presents summary curves for two sets of k tests for brown Sarnia clay moulded and permeated with water/ethanol mixtures at void ratios of 0.8 and 1.2. For both cases, slight viscosity-related decreases in k are noticeable in the low to moderate ethanol concentration range, followed by large values of k as a result of double layer collapse in the highly concentrated range. The corresponding data, adjusted for viscosity/density effects, are shown on Figure 3b as intrinsic permeabilities. Steady increases in K with increasing hydrocarbon content are observed at two distinct slopes, the rate of increase being more pronounced in the high ethanol concentration range. As expected, the values of both k and K are greater at high void ratios than at the lower void ratios. The increases in K are attributed to progressive collapse of the double layers.

Figure 4 shows the results of control tests run with water/ethanol mixtures on reference kaolinite and montmorillonite clays, the former less active and the latter more active than the Sarnia clay. Kaolinite exhibits a viscosity control on k , with little double layer influence at high ethanol concentrations. The very slight increase in K throughout the whole concentration range suggests slight double layer control as the dielectric constant decreases. Montmorillonite, on the other hand, shows some viscosity control on k for ethanol contents of up to 35%, followed by a spectacular rate of increase in both k and K with increasing alcohol content.

The results of tests on Sarnia clay using leachate/ethanol and leachate/dioxane mixtures are presented on Figures 5 and 6. The corresponding tests for water/hydrocarbon mixtures are also plotted.

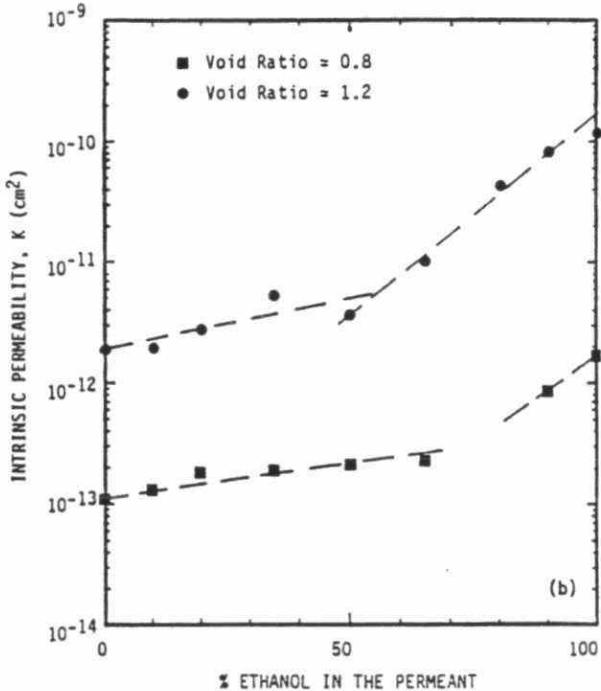
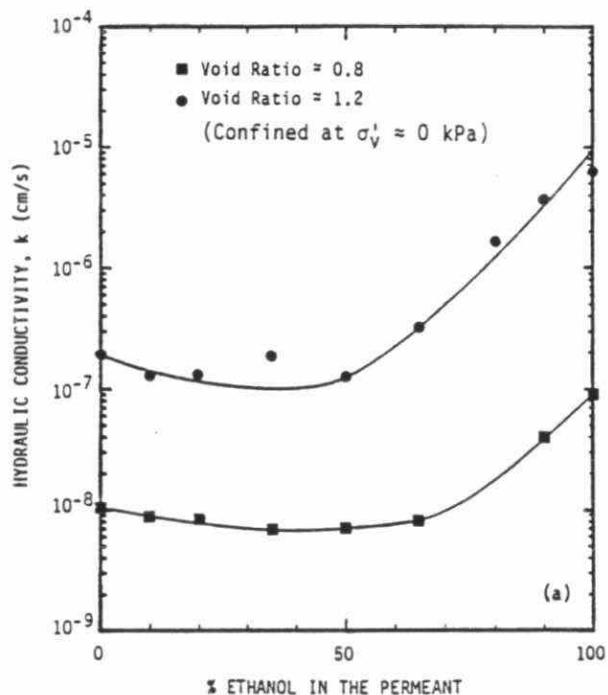


FIGURE 3. HYDRAULIC CONDUCTIVITY (a) AND INTRINSIC PERMEABILITY (b) OF BROWN SARNIA CLAY MOULDED, COMPACTED AND PERMEATED WITH WATER/ETHANOL MIXTURES

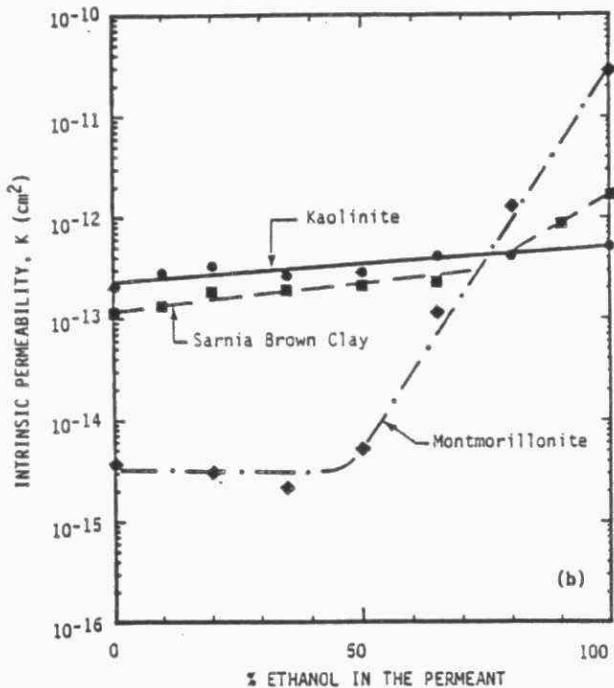
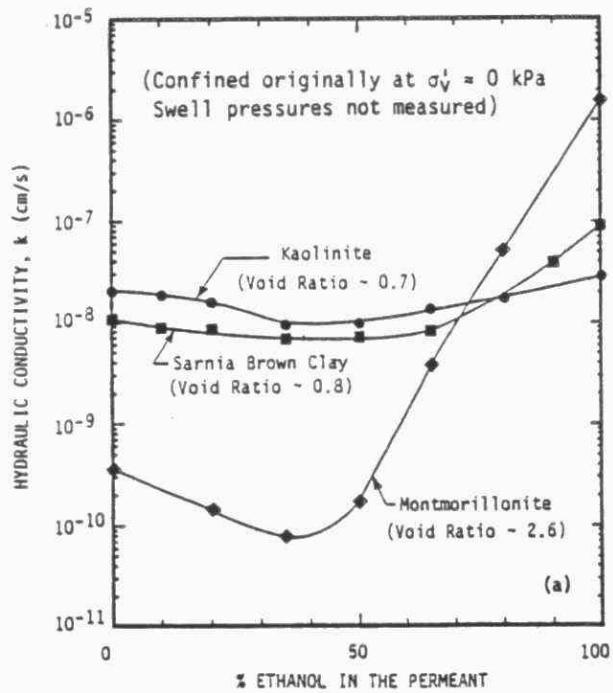


FIGURE 4. HYDRAULIC CONDUCTIVITY (a) AND INTRINSIC PERMEABILITY (b) OF CLAYS MOULDED, COMPACTED AND PERMEATED WITH WATER/ETHANOL MIXTURES

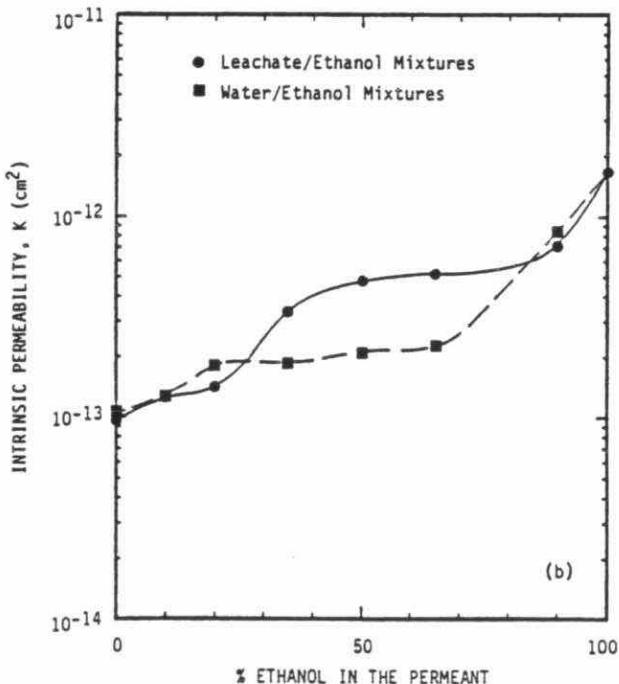
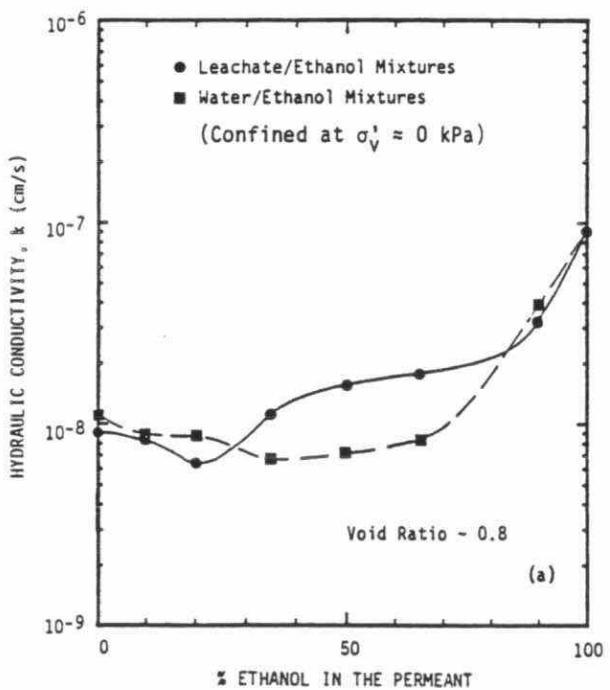


FIGURE 5. HYDRAULIC CONDUCTIVITY (a) AND INTRINSIC PERMEABILITY (b) OF BROWN SARNIA CLAY MOULDED, COMPACTED AND PERMEATED WITH LEACHATE/ETHANOL AND WATER/ETHANOL MIXTURES

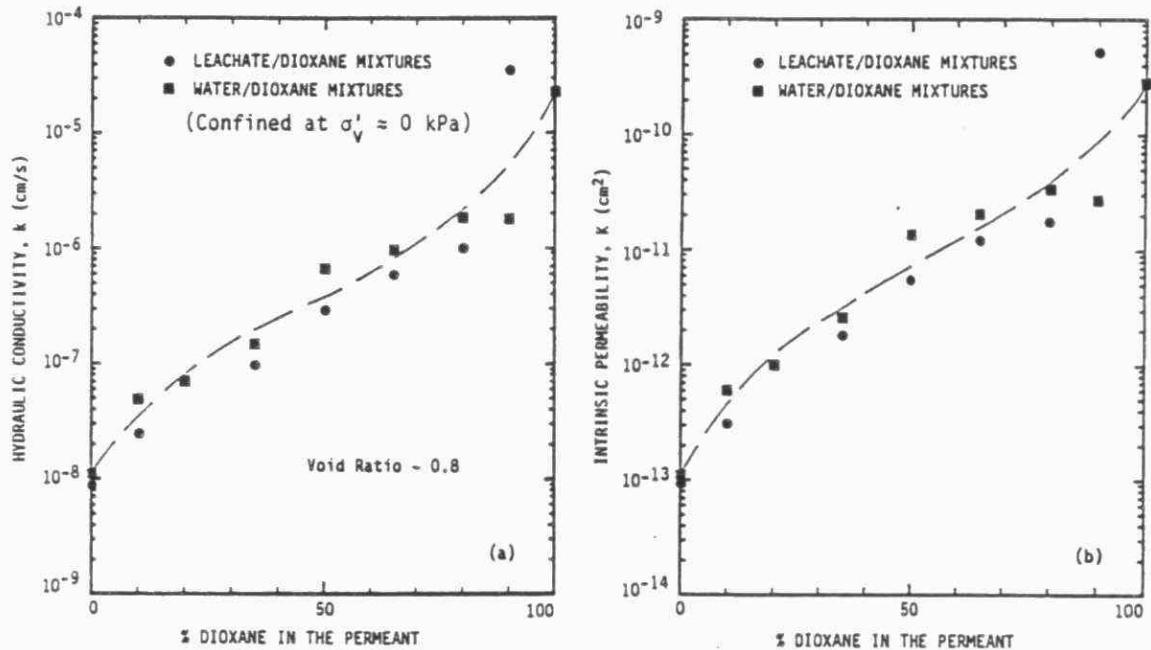


FIGURE 6. HYDRAULIC CONDUCTIVITY (a) AND INTRINSIC PERMEABILITY (b) OF BROWN SARNIA CLAY MOULDED, COMPACTED AND PERMEATED WITH LEACHATE/DIOXANE AND WATER/DIOXANE MIXTURES

The values of k and K are larger for the leachate/ethanol solutions relative to the water solutions in the concentration range of 30% to 60% (Figure 5). In the case of dioxane, no significant differences are evident between the results for leachate and water solutions (Figure 6), however, double layer/fabric effects swamp any viscosity effects and both k and K increase for the entire range of dioxane contents.

The more pronounced increase in k and K for the dioxane mixtures relative to the ethanol mixtures might be expected from their rapidly decreasing values of dielectric constants illustrated on Figure 2.

The pore size distributions determined by mercury intrusion porosimetry on freeze-dried specimens from the leachate/ethanol and water/ethanol samples are shown on Figure 7. Although artifacts created by freeze drying make interpretation risky, the measured variations in dominant pore size seem to exhibit a very close correlation with the values of K plotted on Figure 5b. This suggests that the progressive flocculation of the soil fabric moulded with liquid mixtures of decreasing dielectric constants is responsible for the increases in intrinsic permeability values observed.

HYDRAULIC CONDUCTIVITY TESTS ON WATER-COMPACTED SAMPLES PERMEATED WITH LEACHATE/HYDROCARBON MIXTURES

This section summarizes the hydraulic conductivity studies performed on water-compacted brown Sarnia clays. All samples were permeated with a reference 0.01 N solution of CaSO_4 (water) for ~ 1 pore volume, followed by the leachate/hydrocarbon mixtures of interest. Figure 8 summarizes the hydraulic conductivity test results at $\sigma'_v = 0$ for the samples permeated with leachate containing 0, 20, 40, 60, 80 and 100% ethanol. Reference values for the water (circles) are shown along with final equilibrium values for the permeants (triangles).

Figure 8a shows that significant decreases in k occurred for ethanol contents of up to 60%. The sample permeated with 80% ethanol doubled the k value for water and concentrated ethanol increased k by a factor of more than 100. The test results presented on Figure 8b in terms of intrinsic permeability, show that all permeants containing ethanol produced increases in K relative to water.

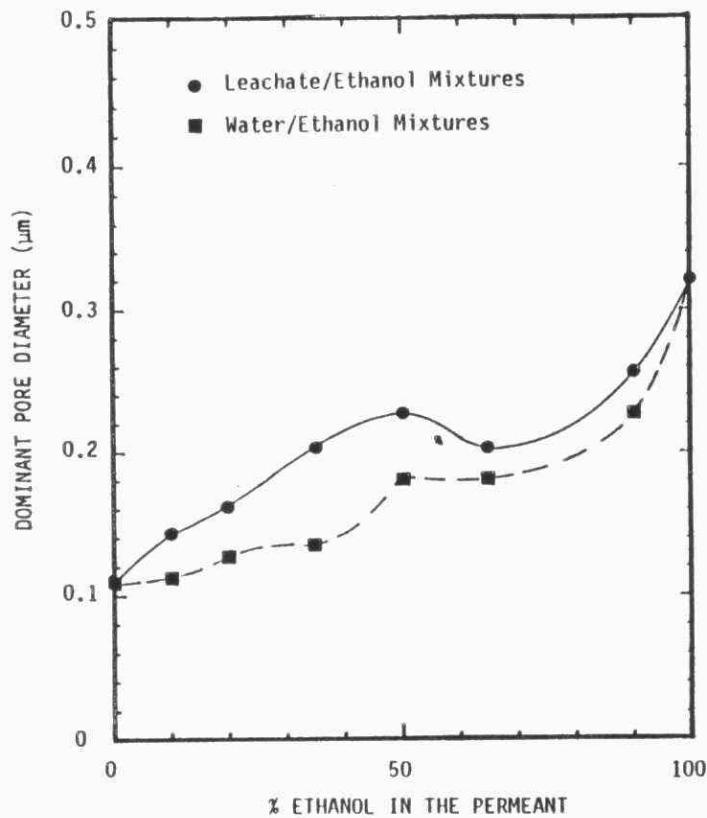


FIGURE 7. DOMINANT PORE DIAMETER IN BROWN SARNIA CLAY SAMPLES MOULDED, COMPACTED AND PERMEATED WITH LEACHATE/ETHANOL AND WATER/ETHANOL MIXTURES (SAME SPECIMENS AS IN FIGURE 5)

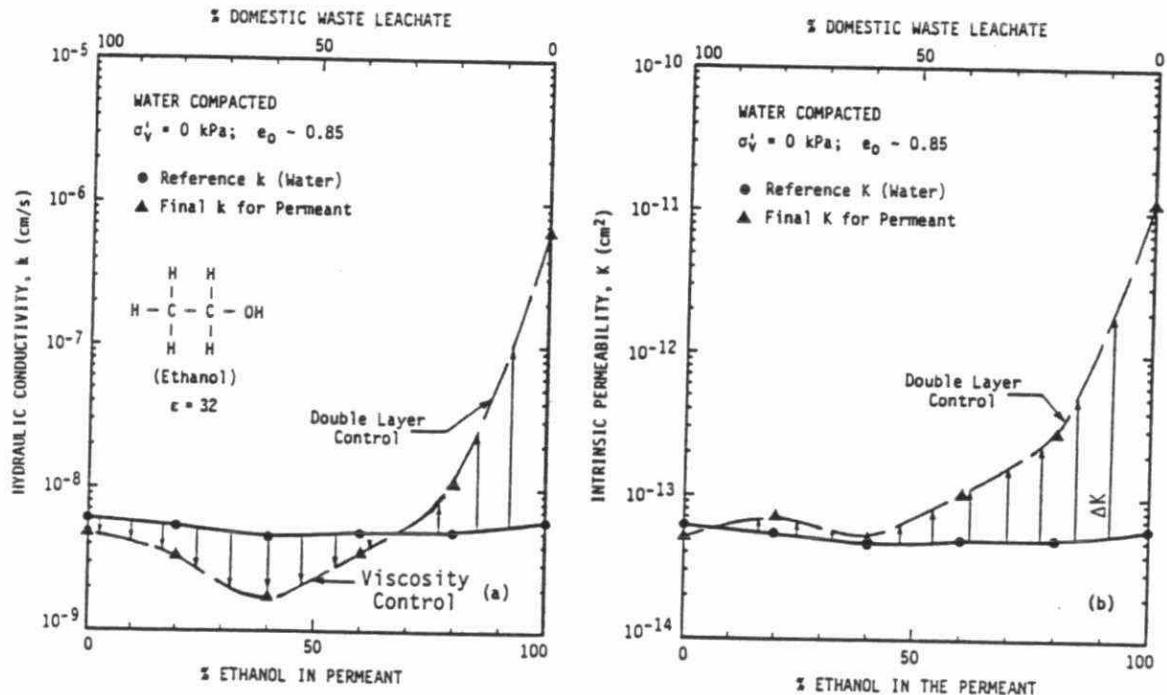


FIGURE 8. HYDRAULIC CONDUCTIVITY (a) AND INTRINSIC PERMEABILITY (b) OF WATER-COMPAKTED BROWN SARNIA CLAY PERMEATED WITH LEACHATE/ETHANOL MIXTURES [All tests run originally with reference water, ●, followed by permeants, ▲, varying from 100% leachate to 100% ethanol]

The magnitude of ΔK appears to increase with the amount of ethanol in the permeant above ~ 50%, reflecting progressive collapse of double layers. It is therefore inferred that the decreases in k observed in the "dilute" concentration range are directly related to the increased viscosity of the permeant.

A second series of hydraulic conductivity tests for samples permeated with leachate containing increasing amounts of dioxane (10, 20, 40, 70, 85 and 100%) are shown on Figure 9. Viscosity-related decreases in k were observed for permeants containing up to 70% dioxane (Figure 9a). The samples permeated with 85% and 100% dioxane, on the other hand, produced increases in k of 2 and 3 orders of magnitude, respectively. The corresponding data expressed as intrinsic permeabilities (Figure 9b) show practically no change in the values of K for dioxane contents of up to 70%. The large increases in K for 85% and 100% dioxane are evidence of double layer contraction in the high concentration range. The strong affinity of double layer cations for water results in exclusion of dioxane molecules at low dioxane contents, preventing the double layer collapse that takes place at high dioxane contents.

Table VI summarizes the results of mercury intrusion porosimetry run on selected specimens from each series of hydraulic conductivity tests. The lack of significant variation in the dominant pore size suggests that the permeants have not altered the fabric of the water-compacted clay samples. The increases in k observed in the concentrated organic range appear to be related to enlargement of the flow channels caused by double layer collapse rather than by increased flocculation of the soil fabric.

Recent evidence of the important role of effective stresses in minimizing the changes in k of clays permeated with concentrated organics has been given by Foreman and Daniel (1986) for flexible wall permeameters and by Fernandez and Quigley (1987) for rigid wall permeameters. In both cases, the application of effective stresses appears to reduce the occurrence of leakage along the sides of the clay specimen. Figures 10 and 11 illustrate the magnitude of this phenomenon for water-compacted brown Sarnia clay permeated with concentrated

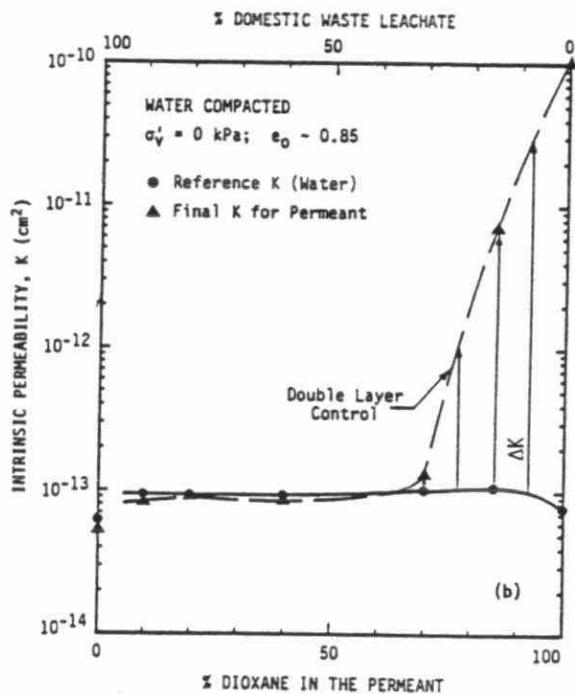
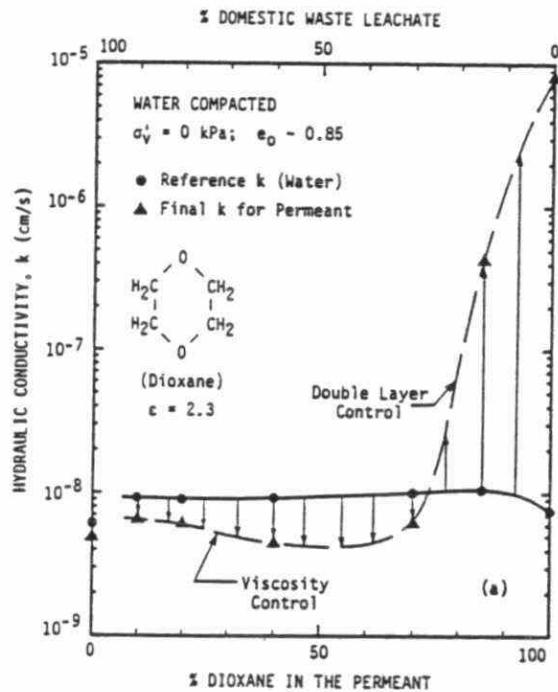


FIGURE 9. HYDRAULIC CONDUCTIVITY (a) AND INTRINSIC PERMEABILITY (b) OF WATER-COMPACTED BROWN SARNIA CLAY PERMEATED WITH LEACHATE/DIOXANE MIXTURES [All tests run originally with reference water, ●, followed by permeants, ▲, varying from 100% leachate to 100% dioxane]

dioxane and ethanol. The reference or original values of k corresponding to 1 pore volume of water permeation (Figure 10) vary from 6.25×10^{-9} cm/s at $\sigma'_v = 0$ kPa to 3.9×10^{-9} cm/s at $\sigma'_v = 160$ kPa. Subsequent permeation with pure dioxane resulted in increases in k , with the magnitudes inversely proportional to the applied effective stresses. Consolidation during dioxane permeation at $\sigma'_v = 160$ kPa amounted to 1.5% of the total volume of the sample, resulting in smaller increase in k due to pore closure. Also, the effective stresses improve the contact between the clay and the rigid walls of the permeability cells due to K_0 effects, reducing side wall flow. Figure 11 shows that the application of a vertical effective stress, σ'_v , of only 40 kPa successfully prevents any increase in k during permeation of concentrated ethanol, compared to the 100-fold increase at $\sigma'_v = 0$ kPa. In fact, the final value of k after ethanol permeation at $\sigma'_v = 40$ kPa is slightly lower than the reference value for water, which is partly attributed to the higher viscosity of the permeant ($\nu = 1.8$ centistoke).

Finally, it is significant that the curves corresponding to the higher effective stresses on Figures 10 and 11 ($\sigma'_v = 160$ and 40 kPa, respectively) both show initial decreases in k from the value for water, followed by gradual increases in k as the test progresses. The increased viscosity in the pore fluid as the permeant disperses into the sample produces the drop in k . As the test progresses the organics in the pore fluid become more concentrated, reducing its viscosity (Figure 1), and double layer control on k becomes more noticeable. Similar patterns of variations in k can be seen in tests run with concentrated water-soluble organics reported by other authors (Anderson and Brown, 1981; Green et al., 1981; Acar et al., 1985; Anderson et al., 1985; Acar, 1987).

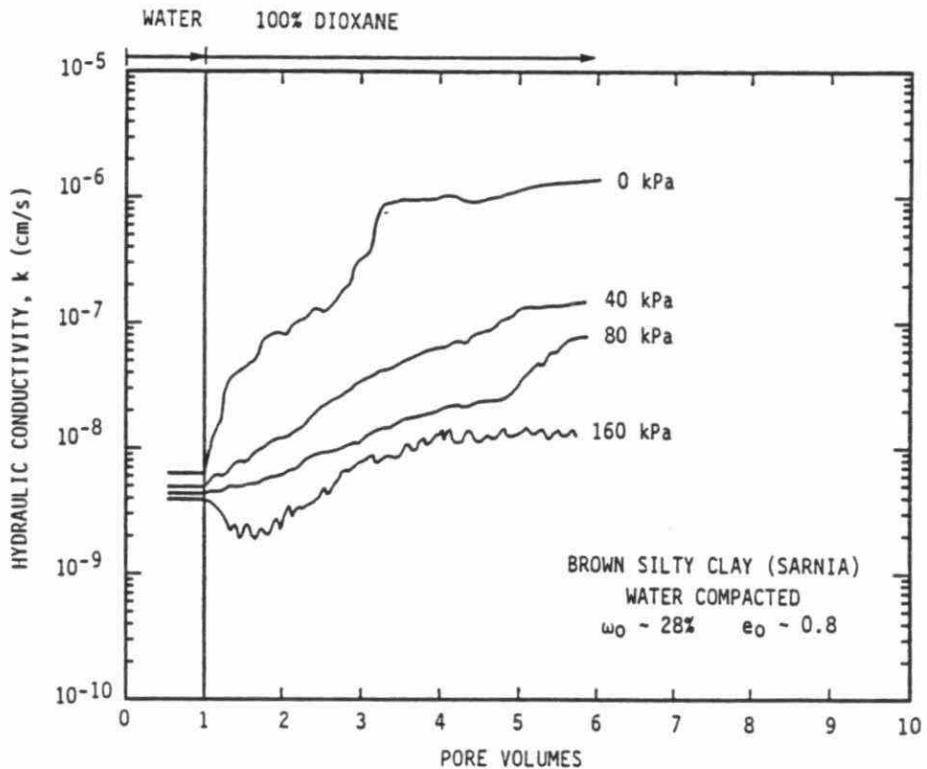


FIGURE 10. HYDRAULIC CONDUCTIVITY VS PORE VOLUMES FOR WATER-COMPACTED BROWN SARNIA CLAY PERMEATED WITH 100% DIOXANE USING VERTICAL EFFECTIVE STRESSES OF 0, 40, 80 AND 160 kPa

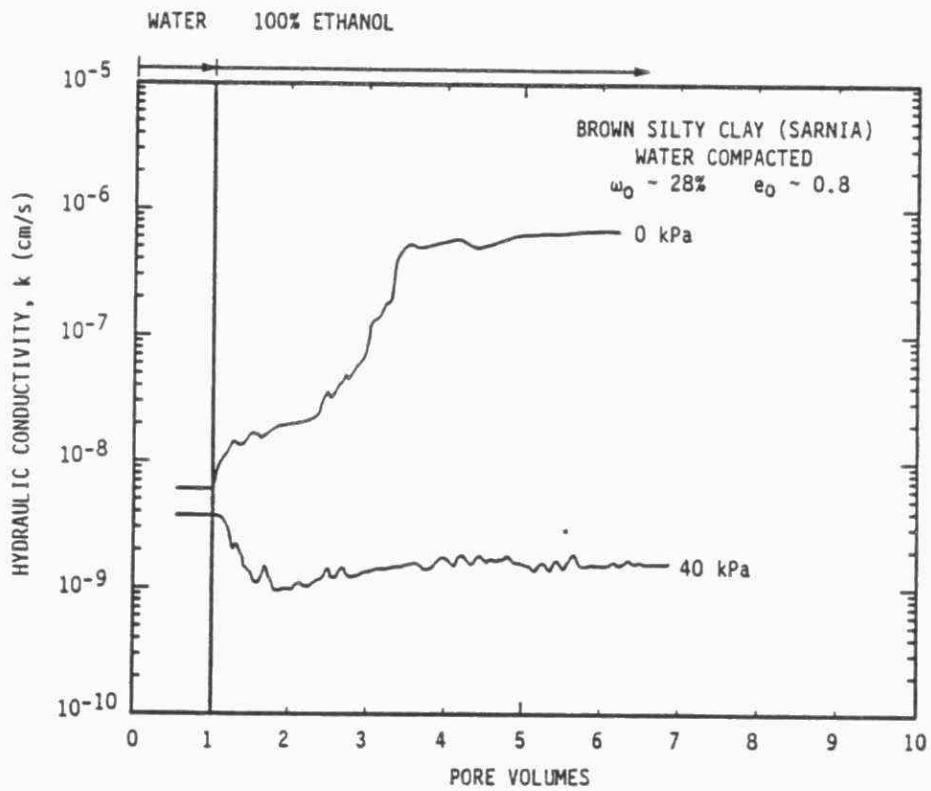


FIGURE 11. HYDRAULIC CONDUCTIVITY VS PORE VOLUMES FOR WATER-COMPACTED BROWN SARNIA CLAY PERMEATED WITH 100% ETHANOL* USING VERTICAL EFFECTIVE STRESSES OF 0 AND 40 kPa
[* Commercial grade ethanol (95% absolute)]

CONCLUSIONS

The following conclusions may be drawn from the work presented in this paper on aqueous solutions or organics and the hydraulic conductivity of clays.

I. Water-Compacted Clays

- 1) Viscosity-related decreases in k occur for both ethanol and dioxane solutions up to concentrations of 70%.
- 2) Permeants containing ethanol or dioxane in excess of 80% may produce large increases in k in the absence of an applied effective stress.
- 3) Effective stresses causing vertical consolidation and K_0 related shear stresses reduce or eliminate the increases in k for concentrated organics.

II. Dried Clays Moulded with the Permeants

- 1) The flocculation of the soil fabric during sample preparation (mixing and compaction) reflects the double layer effect and correlates very closely with the variations in intrinsic permeability (pore size distribution data).
- 2) Less active clay (kaolinite): k mainly controlled by permeant viscosity. Most active clay (montmorillonite): k exhibits a spectacular double layer control. Sarnia clay behaves in between.
- 3) The laboratory study suggests that moulding of clays in the field with the probable permeant will generate higher k values and is not an acceptable procedure.

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TABLE I. DENSITY AND VISCOSITY OF WATER/ETHANOL MIXTURES
(all values measured at 20°C)

Ethanol Content (% by wt) ⁽¹⁾	Density ρ (g/cm ³)	Dynamic Viscosity μ (centipoise)	Kinematic Viscosity ν (centistoke)
0	1.00123	1.00123	1.00000
10	0.98429	1.43892	1.46189
20	0.97223	2.00342	2.06064
35	0.95082	2.59662	2.73093
50	0.92297	2.71435	2.94088
65	0.89128	2.49363	2.79781
80	0.85762	2.09202	2.43933
90	0.83463	1.74463	2.15317
100	0.81026	1.46300	1.80559

Note: (1) Commercial grade ethanol containing up to 5% water.

TABLE II. DENSITY AND VISCOSITY OF WATER/DIOXANE MIXTURES
(all values measured at 20°C)

Dioxane Content (% by wt)	Density ρ (g/cm ³)	Dynamic Viscosity μ (centipoise)	Kinematic Viscosity ν (centistoke)
0	1.00123	1.00123	1.00000
10	1.00807	1.20999	1.20031
20	1.01640	1.43455	1.41140
35	1.02568	1.77479	1.73035
50	1.03398	2.09823	2.02928
65	1.04008	2.16991	2.08629
80	1.03920	1.88785	1.81664
90	1.03830	1.55825	1.50077
100	1.03373	1.27970	1.23795

TABLE III. DENSITY AND VISCOSITY OF LEACHATE/ETHANOL MIXTURES
(all values measured at 20°C)

Ethanol ⁽¹⁾ Content (% by wt)	Density ρ (g/cm ³)	Dynamic Viscosity μ (centipoise)	Kinematic Viscosity ν (centistoke)
0	1.00405	1.05089	1.04665
10	0.98901	1.46447	1.48074
20	0.97347	2.11194	2.16949
35	0.93643	2.76456	2.95223
50	0.90458	2.71513	3.00154
65	0.89094	2.56162	2.87519
80	0.85901	2.17995	2.53775
90	0.83622	1.82319	2.18028
100	0.81026	1.46300	1.80559

Note: (1) Commercial grade ethanol containing up to 5% water.

TABLE IV. DENSITY AND VISCOSITY OF LEACHATE/DIOXANE MIXTURES
(all values measured at 20°C)

Dioxane Content (% by wt)	Density ρ (g/cm ³)	Dynamic Viscosity μ (centipoise)	Kinematic Viscosity ν (centistoke)
0	1.00405	1.05089	1.04665
10	1.01150	1.28758	1.27294
20	1.01914	1.51365	1.48523
40	1.03164	1.97022	1.90980
70	1.04194	2.16976	2.08243
90	1.03549	1.57444	1.52048
100	1.03373	1.27970	1.23795

TABLE V. DIELECTRIC CONSTANT OF WATER/ETHANOL
AND WATER/DIOXANE MIXTURES

(all values measured at room temperature, 22-24°C)

Hydrocarbon Content (% by wt)	Dielectric Constant	
	(1) Water/Ethanol	Water/Dioxane
0	83.6	83.6
10	78.9	68.8
20	73.8	60.5
35	65.3	47.1
50	56.1	33.5
65	47.7	20.5
80	40.5	9.06
90	36.2	6.02
100	32.1 ⁽²⁾	2.26

Notes: (1) Commercial grade ethanol containing up to 5% water.

(2) Dielectric constant for pure ethanol = 25.0.

TABLE VI. DOMINANT PORE DIAMETER FOR WATER-COMPACTED BROWN SARNIA CLAYS PERMEATED WITH LEACHATE/HYDROCARBON MIXTURES

Permeant	Dominant Pore Diameter (μm)
80% Leachate 20% Ethanol	0.08
60% Leachate 40% Ethanol	0.08
100% Ethanol	0.08
90% Leachate 10% Dioxane	0.10
80% Leachate 20% Dioxane	0.18
60% Leachate 40% Dioxane	0.11
30% Leachate 70% Dioxane	0.09
100% Dioxane	0.08

EVALUATION OF CONTAMINANT VELOCITY IN
LOW-PERMEABILITY FRACTURED SHALE

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INTRODUCTION

The prediction of subsurface migration of toxic contaminants from landfills disposal or industrial sites underlain by fractured shale has become an important consideration in the assessment of water quality in the heavily-industrialized regions of southern Ontario. For example, the near-surface sediments of the Oakville-Mississauga region are underlain by the fractured Dundas shale, the Burlington-Hamilton region has the Queenston and Rochester shales, and the Niagara Falls region has various fractured shales including the Queenston shale that may transmit contaminants through the subsurface to the Niagara River. Because fractured shale with low matrix permeability underlies much of these industrialized regions, it is probable that fractures will play an important, if not dominant role, in providing pathways for subsurface migration of toxic contaminants. This leads to the expectation that very large contaminant plumes can develop within fractured shale under conditions of relatively low contaminant mass flux into the shale. Consequently, landfills and industrial sites situated on fractured shale can produce large plumes of contaminated groundwater that extend over considerable distances. Risk assessments for the design, siting, or clean up of such sites require that hydrogeologic models be used to estimate the extent and rates at which contaminants may migrate from the site to the accessible biosphere. The most important step in predicting the extent to which groundwater contamination could occur is the determination of the average velocity of the non-reactive contaminants. In groundwater investigations, however, the greatest difficulties and uncertainties in measuring and modelling groundwater velocities occur in fractured rock.

There are two modelling approaches to the simulation of fluid flow and contaminant transport in fractured media. The continuum approach treats a fractured rock mass as if it were equivalent to a porous medium, while network models are based upon an explicit representation of the fractures. If fracture densities are much greater than those that mark the onset of percolation, then a continuum approach can be adopted. In this case, parameters must be formulated to characterize advective, dispersive, and chemical processes occurring within representative elemental volumes (REV) of the fractured shale mass. At sites underlain by sparsely fractured shale, or those where a significant proportion of the fractures are sealed by mineral precipitates, considerable transport distance may be required before contaminants encounter a representative sample of fluid velocities. Until contaminants have migrated over that distance, continuum models are not applicable. It is also conceivable that there may be several scales of fracturing within the flow region, with a relatively few, areally extensive fractures exerting a disproportionately large influence on the groundwater flow velocities. These situations can be identified as sub-REV problems where discrete network models are appropriate. A characteristic of such sites is the potential for contaminant transport to be significantly influenced by individual fractures and their interconnections with other fractures forming the network.

Migration of contaminants in a network of discrete fractures that cannot be represented using a continuum approach, including the region close to the site where contaminants enter the flow system, can be simulated using stochastic modelling techniques. The starting point for a stochastic model is a statistical description of fracture geometry. Probability descriptions of the fracture locations, dimensions, and apertures are required to transform a geometrical model of the fracture network into a hydraulic model. Although stochastic fracture models are powerful analytical tools, if they are to find practical applications, then it is necessary to demonstrate that reliable estimates of model parameters can be obtained within the normal constraints of field investigations. One key parameter is fracture aperture. Mechanical measurements of aperture in the disturbed region around a borehole are of questionable reliability. Current practice relies on hydraulic and, or, tracer tests to obtain in situ estimates of fracture aperture. From measurements of aperture and hydraulic head, it is then possible to calculate the groundwater velocity in the fracture. The objective of this study is threefold. First, to examine numerically the reliability of several hydraulic and induced-gradient tracer tests used to obtain in situ estimates of fracture aperture. Second, to apply these tests in the determination of the aperture of a fracture zone within low-permeability shale at a specific field site. Third, in light of the errors inherent in the interpretation of hydraulic and tracer tests, to assess whether the groundwater velocity determined from the estimated aperture and measurements of hydraulic head correctly represents the in situ velocity in the fracture. In this paper we discuss results from the first objective, numerical simulation of hydraulic and tracer tests. Preliminary results for the in situ determination of aperture and groundwater velocity for a specific field site are presented in the later part of the paper.

ESTIMATION OF FRACTURE APERTURE

Estimates of fracture aperture can be derived from both hydraulic and tracer tests. While a variety of testing configurations are possible, the examples presented here focus on steady state withdrawal tests. In this approach, a section of borehole adjacent to the fracture identified for testing is isolated and water is withdrawn from the fracture by pumping at a constant rate Q . Flow patterns and the groundwater velocity field within the fracture will depend upon how fluid moves in from the far-field to meet the pumping demand. Once steady state conditions are established, the fracture aperture can be estimated from difference in hydraulic head between an observation well and the withdrawal well. If a tracer is released from an observation well, then the aperture can also be estimated from its travel time to the withdrawal well. Examples of a withdrawal tests are given by Hodgkinson and Lever (1983), Abelin et al. (1985), Novakowski et al. (1985), and Anderson and Thunvik (1986).

To estimate fracture aperture, a model must be adopted to describe the flow field within the fracture plane. Models based on an assumption of axisymmetric flow are commonly used. Three such steady-state models are examined here. All three approaches are deterministic and have been adapted from methods originally used for interpreting hydraulic and tracer tests carried out in confined aquifers.

Assuming axisymmetric flow toward the withdrawal well, the volume flux across a surface a distance r from the withdrawal well is related to the pumping rate by

$$(1) \quad Q = 2\pi K_f b \frac{dh}{dr}$$

K_f is the equivalent hydraulic conductivity of the fracture plane and b is the fracture aperture. Adopting Poiseuille's equation for laminar flow in a parallel plate opening of aperture b , and given values of hydraulic head at radial distances r_o and r_w , the fracture aperture is given by

$$(2) \quad b_h = \left[\frac{Q}{(h_o - h_w)} \frac{6\mu}{\pi p g} \ln(r_o/r_w) \right]^{1/2}$$

where b_h is referred to as the 'hydraulic aperture', r_w is the well radius and $(h_o - h_w)$ is the measured difference in hydraulic head between the observation and withdrawal wells.

A second model to estimate fracture aperture is based on mass balance considerations. For a tracer to move by advection from r_o to r_w , the fluid volume contained between the two radii r_w and r_o must be removed by the pumping well. If t_w denotes the travel time of a tracer from r_o to r_w , then the volume of water pumped in time t_w is given by

$$(3) \quad Qt_w = \pi b (r_o^2 - r_w^2)$$

The fracture aperture is estimated from (2) by

$$(4) \quad b_v = \frac{Q t_w}{\pi (r_o^2 - r_w^2)}$$

where b_v is referred to as the 'volume balance' aperture. In making this calculation, the area from which fluid is withdrawn is given implicitly by the radial distance from the injection point (r_o) to the outer radius of the withdrawal well (r_w).

A third approach for estimating fracture aperture also uses results from tracer tests. The travel time from an injection point to the withdrawal well is given by

$$(5) \quad t_w = \int_{r_o}^{r_w} \frac{dl}{v_i}$$

where the integration is along the streamline connecting the injection point with the withdrawal well and v_i is the groundwater velocity along the streamline. In general, both the path length and the variation in the advective velocity along the streamline are unknown. By expressing the travel time as a function of an assumed axisymmetric flow in a parallel-plate fracture, both the path length and the radial velocity are known to within a constant that is given by the fracture aperture. The aperture is calculated by

$$(6) \quad b_t = [\frac{6 \mu \ln(r_o/r_w)}{\rho g t_w (h_o - h_w)} (r_o^2 - r_w^2)]^{1/2}$$

where b_t is referred to as the 'tracer aperture'.

All three models are appropriate for the idealized case of laminar flow in a smooth, planar fracture of large areal extent. It is important to recognize that these simple axisymmetric models are adopted in practice because data are seldom, if ever, available to refine the specification of boundaries on the fracture plane and on source or sink positions. However, the potential exists for deviations from these simple models because of distortion of the flow field by the roughness of the fracture walls, fractures with finite dimensions, and fracture intersections that act as line sources or sinks of fluid. In the following sections, we describe a numerical experiment that examines the magnitude of potential errors in the interpretation of hydraulic and tracer tests to obtain estimates of fracture aperture. The numerical model used here is described by Smith et al. (1985). This model simulates fluid flow and contaminant transport in three-dimensional networks of discontinuous, rough-walled fractures. Variations in aperture within each planar fracture could depend upon a number of factors including the roughness of fracture walls, the distribution of fracture-filling material, and fracture closure due to an applied stress. Differences between the in situ numerical aperture, and the estimated aperture based on hydraulic and travel time data are highlighted. In the following example, it is assumed that two boreholes penetrate a fracture which is identified for field

testing. The numerical experiment focuses on the factors that distort the radial flow field. To focus on these factors, matrix diffusion is neglected and the validity of the cubic law is not examined. We view these as important but separate issues.

Example of an Injection-Withdrawal Test

Figure 1 illustrates a fracture network positioned within an impermeable rock block. This section represents a vertical slice through the center of the rock mass. The network consists of three horizontal fractures, connected by ten cross fractures that intersect the horizontal fractures at 60°. Tests are simulated assuming the injection and withdrawal boreholes are open only to fracture plane two. The bounding edges of this fracture are impermeable. The withdrawal well is located at the center of fracture plane with a withdrawal rate of 0.8 l/min. Fracture planes one and three extend to external boundaries and are assigned equal values of hydraulic head on the X face. Water moves in from these constant head boundaries to meet the pumping demand of the withdrawal well. The Y face of the block is impermeable. Although highly idealized, this network contains features characteristic of the selected field site that can be expected to perturb an axisymmetric flow field. Solutions for the hydraulic head distribution and contaminant travel time through this three-dimensional network are obtained using a model described by Smith et al. (1985, 1986). In general, other examples show that the volume balance aperture is not a reliable estimate because of its sensitivity to errors in the assumed geometry of the region where water is withdrawn. Consequently, we will not consider it for this example.

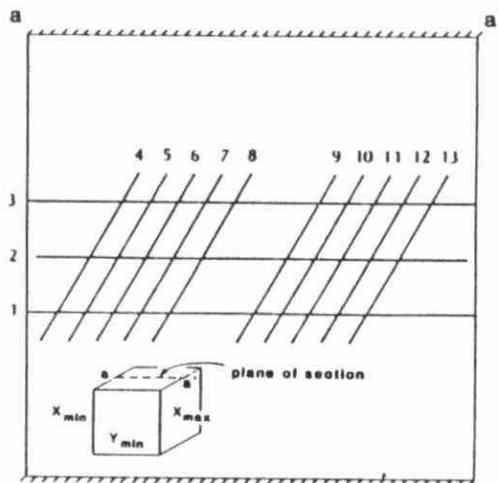


Figure 1. Discrete fracture network used in numerical simulations.
Domain is 16 x 16 x 16 M.

Field evidence suggests that even for "open" fractures, there is considerable variation in the aperture of a planar fractures, due to combined effects of undulating fracture surfaces, mineral precipitates, and closure under in situ stresses. This aperture variation leads naturally to concepts of "channelling" within a fracture network. To model rough-walled, open fractures, aperture values can be represented as a spatial stochastic process. Results for a single realization are described here. For the horizontal fractures and cross fracture twelve, a lognormal distribution is specified with a log mean of -3.30 and a log standard deviation of 0.25 (base ten logarithms for aperture in meters). An isotropic correlation length of 2 m is assumed. Aperture values for the remaining cross fractures are generated from $\text{LOG}(-5.50, 0.25)$. Thus fracture twelve forms the dominant link between fracture plane two and the other fractures within the network. Values of the standard deviation and correlation length are selected here only to illustrate concepts, and do not represent a particular geologic environment. Figure 2a is a contour plot of the aperture variation within fracture plane two. Note that there is a crescent-shaped channel of higher aperture located within the central region of the fracture plane.

Figure 2b is a plot of the steady state hydraulic head field within fracture plane two. The values shown have been normalized, with the hydraulic head at the withdrawal well assigned a value of zero, and the maximum hydraulic head within the fracture plane assigned a value of one. The plot demonstrates that the general pattern of groundwater flow is determined by the geometry of the fracture network and the connections to the constant head boundaries, with the aperture variation acting to perturb the magnitude of the local hydraulic gradient. Due to the influence of the geometry of the network and the roughness of the fracture walls the flow field is decidedly non-symmetric.

A plot of hydraulic aperture is shown in Figure 2c. In this figure, the aperture values at a specific point on the fracture plane represent the aperture which would be calculated from a hydraulic tracer test if the observation well were located at that point. The plot is constructed by specifying a regularly-spaced grid of well locations, noting the hydraulic head at each location, and using a tracking particle to trace the path and travel time from each observation well point to the withdrawal well. From this data, both the hydraulic and tracer apertures can be calculated. Two features can be noted. First, the hydraulic aperture is insensitive to the spatial variability in aperture within the fracture plane. Second, the magnitude of the hydraulic aperture is primarily influenced by aperture values in the close vicinity of the withdrawal well. This happens because it is also the region where the greatest drop in hydraulic head occurs. To illustrate this effect, Figure 2e is a plot of the hydraulic aperture calculated for the same fracture. The withdrawal well, however, is now located in a region where the fracture aperture is approximately 200 microns. For this case, the hydraulic head is much lower, again reflecting the real value close to the withdrawal well. Other examples, not shown here, suggest the hydraulic aperture is only mildly sensitive to the distortion of a radial flow field due to network effects, fracture intersections.

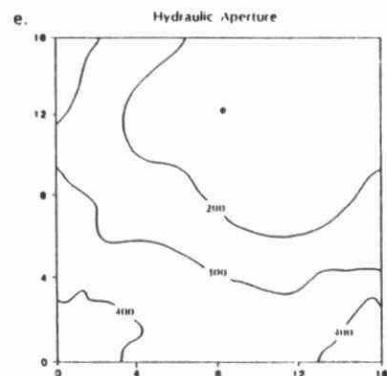
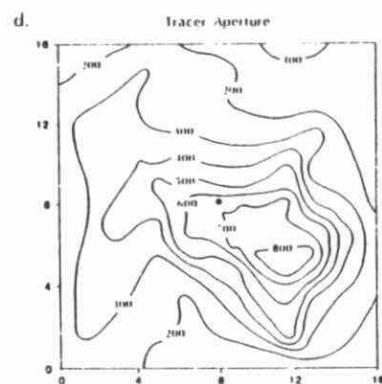
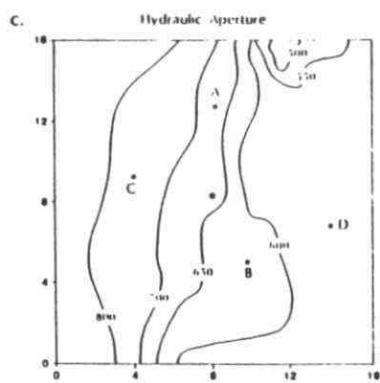
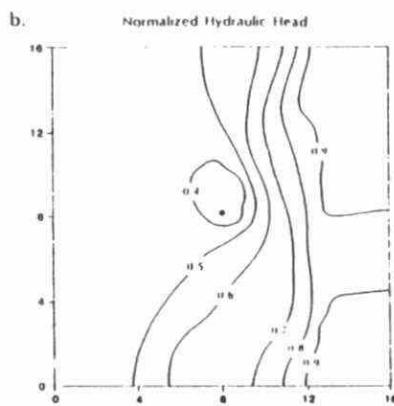
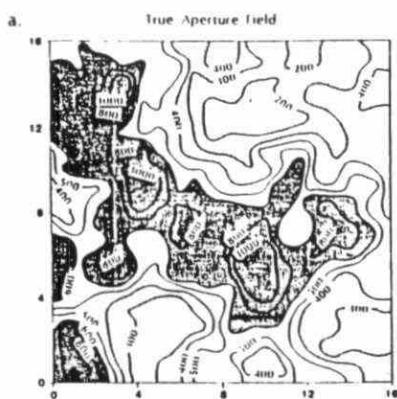


Figure 2. Results of aperture calculations for fracture plane two, network of rough-walled fractures. Aperture values are in microns.

Values of the tracer aperture for the same fracture are shown in Figure 2d. The tracer aperture is sensitive to the location of fracture intersections that provide water to meet the pumping demands, and to the relative position of the lower and higher aperture zones within the fracture plane. Calculated apertures are a smooth version of real values. The higher aperture region between the withdrawal well and the fracture intersection is identified, although estimated values are significantly less than peak values. The extension of this 'channel' into the region behind the fracture intersection or on the opposite side of the withdrawal well is not identified because of the limited groundwater flow which occurs there.

Figures 2c and 2d can be compared to identify relationships between aperture estimates based on hydraulic and tracer data. Consider the position of observation wells at points labelled A, B, C, and D. Point A is located within a region of the fracture plane with a lower aperture than the mean value. Here the estimate of hydraulic aperture exceeds the tracer aperture by a factor of three. The hydraulic head does not record the lower aperture zone because this model primarily reflects conditions only in the immediate vicinity of the withdrawal well. In general, the hydraulic aperture will exceed the tracer aperture if the withdrawal well is located in a more permeable zone of the fracture plane than the observation well. A tracer released at point A traverses the low aperture zone and thereby records a longer travel time, leading to the lower value of tracer aperture. At point B, estimates of the tracer aperture would exceed the hydraulic aperture by approximately 200 microns because the observation well is located in a zone with a greater aperture than the withdrawal well, and its position in the main 'channel' that supplies groundwater to the withdrawal well. At points C and D, the hydraulic aperture exceeds the value estimated from a tracer test. At point C, the tracer aperture is less than one third the real value because most of the water withdrawn for the well comes from the fracture intersection located on the other side of the well. Consequently, the slow 'back circulation' in this half of the fracture leads to large travel times and aperture estimates. For point D, the tracer aperture underestimates the real value because limited circulation within the dead-end segments of the fracture plane leads to large travel times and, consequently, lower estimated apertures. The hydraulic aperture, however, reflects the hydraulic head along the fracture intersection of the dead-end fracture fracture and thereby does not feel the effects of large travel times from this region.

The example presented here demonstrates the potential for errors in estimates of fracture aperture using conventional testing and interpretational procedures. Large differences between hydraulic and tracer apertures are possible because of differing sensitivities to the effects of spatial variations in aperture within a fracture plane, and the presence of fracture intersections due to network geometry. In field operations, however, such information to aid in the interpretation of field data is seldom, if ever, available. If reliable estimates of fracture apertures are to be derived from the field results of hydraulic and tracer tests, it appears that an approach is needed to provide for additional constraints on the model adopted to describe the groundwater

flow system. Such techniques conceivably require multiple borehole responses, more sophisticated interpretational models than those based on simple axisymmetric flow, integration with geophysical techniques that sense the migration of a tracer within a fracture plane or network, or measurement of the in situ groundwater velocity by means of borehole dilution or natural-gradient tracer tests.

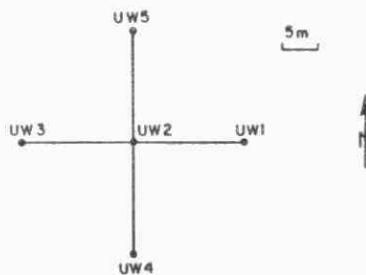
STUDY SITE

A site on Petro-Canada property in Clarkson, Ontario was selected to evaluate and compare several methods for determination of the groundwater flow velocity in fractured shale. The site was selected for three main reasons. First, it is located on the Dundas shale, a fractured low-permeability shale hydrologically similar to other shale deposits of southern Ontario. Second, background information on the hydrogeology was available indicating a shallow water table, thin overburden (2 m), and flat lying bedrock. Finally, the site has easy access and is a secure site with respect to long-term monitoring and limited potential for vandalism. The ultimate aim for the site is to predict the migration of an injected tracer in a single fracture, and compare the predicted concentrations with the actual measured values in the fracture.

A preliminary drilling program was conducted in May 1986, and five boreholes were drilled 15 m apart in two perpendicular rows of three as shown in Figure 3. The boreholes were continuously cored using an NV3 core barrel, and were drilled in the following manner. Hollow stem augers were advanced until refusal in the weathered bedrock at approximately 3 m. The boreholes were then drilled by triconing to a depth of approximately 5.5 m, and then cored to 16.5 m below ground surface at each location. The core was logged in the field and photographed in 60 cm sections. Once the drilling was completed, casing was set to a depth of 5 m and the borehole was left open to allow for downhole testing.

The core consisted primarily of shale with interbedded dolomite layers approximately 5-20 cm thick. The fracture pattern is primarily horizontal (along bedding planes) in the shale and vertical in the dolomite. The degree of fracturing generally decreased with depth. Examination of the core and subsequent packer tests delineated several high-permeability zones. The location of these main fracture zones were correlated between each borehole to determine which fractures zones could be continuous across the site. Four main fracture zones were delineated at depths of 6.5-6.8, 7.2-7.6, 10.4-10.7, and 14.0-14.3 m below the ground surface. The fracture zones were isolated using a double packer assembly which was pneumatically inflated with nitrogen. Water was then injected into the isolated zones at a constant pressure and the injection rate monitored. Results of packer testing indicated that the zone of highest permeability is located at depths of 10.4-10.7 m. The other zones tested exhibited a lower apparent permeability, and exhibited a decrease in the injection rate as the test continued. This decrease suggests that these fracture zones are localized and not continuous in lateral extent across the field site. Packer tests in non-fractured shale above and below the most permeable zone suggest a hydraulic conductivity of less than 10^{-10} ms^{-1} .

PLAN VIEW



PIEZOMETRIC SURFACE - ISOMETRIC SKETCH

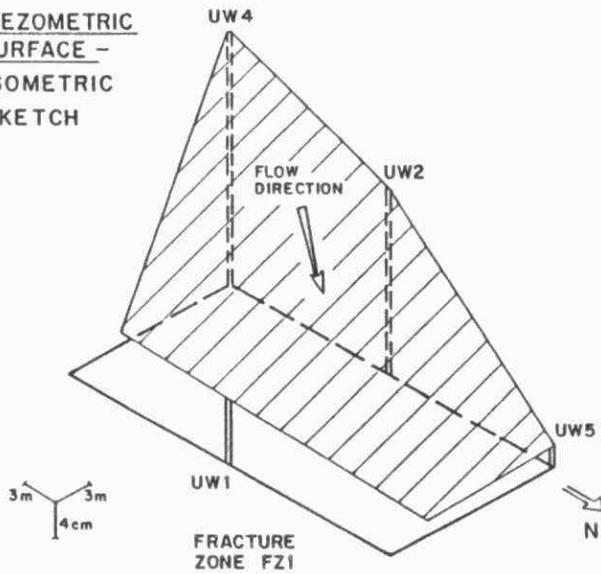


Figure 3. Plan view and hydraulic head surface of FZ1 at the Clarkson site.

Subsequent field work in the summer of 1987 focused on the most permeable zone (FZ1) located between 10.4-10.7 m depths. The objective of this work was to characterize the hydraulic head and fracture aperture within FZ1, and then use this data to predict groundwater velocities in FZ1. To measure the hydraulic head in FZ1, the zone was isolated in all boreholes by inflation of four triple packer piezometers. Problems were encountered in obtaining a stable set of measurements since deflation of a single packer would hydraulically connected FZ1 with other fracture zones. The packers were initially prone to slow leaks either through the rubber packer seals or poorly sealed valves and fittings. Due to these difficulties only one reliable set of measurements were obtained. Figure 3 shows a plan view of the site, together with an isometric diagram of the hydraulic head within FZ1 as viewed from the northeast. The hydraulic head in UW1, UW2, UW4, and UW5 ranged between 5.53 and 5.61 m below ground surface. Measurements in UW3, however, indicated a head of 3.23 m. Because of suspected packer problems, the measured hydraulic head at UW3 was not used for calculating the hydraulic gradient. The calculated hydraulic gradient based on the remaining wells is 0.01 and is towards the Northeast. The regional gradient is almost certainly to the Southeast towards Lake Ontario. Hydraulic head distributions in fractured rock, however, are usually complex. It is, therefore, not unusual to find groundwater flowing in a direction different from the regional gradient at such a shallow depth and small scale of observation (30 m).

A five hour pump test with a withdrawal rate of 460 ml min^{-1} from borehole UW5 produced drawdown in the remaining four observation wells. The drawdown data show a typical Theis behaviour with no apparent boundary effects and suggest that FZ1 is one continuous fracture zone with no lateral boundaries close to the site. In addition, none of upper packed off intervals above FZ1 registered any change in hydraulic head during the test which suggests that no vertical connections exists with other high-permeability zones. Fracture apertures calculated using equation (2) indicated an average hydraulic aperture of $160 \mu\text{m}$ with a standard deviation of 38 ($\text{LOG}(2.19, .11)$). Similar aperture values are calculated from the hydraulic transmissivity obtained from a Theis analysis of the drawdown data. Such values, however, should be viewed with caution because well bore storage effects can cause the Theis method to underestimate the fracture transmissivity (Raven, 1986).

As seen from the previous numerical example (Figure 2), changing the position of the pumping well would yield substantially more information on the fracture aperture within FZ1. The average aperture of $160 \mu\text{m}$ may reflect the aperture immediately surrounding well UW5, or it may reflect a relatively uniform aperture within FZ1. Later this fall we expect to move the position of the withdrawal well to each of the remaining four wells in turn and thereby obtain a set of four hydraulic-aperture measurements for each well. Variations in aperture within these sets should give us a clue to the variation in aperture within FZ1. In addition, preliminary induced-gradient tracer tests are expected to be carried out. From these tests, the volume balance and tracer apertures (equation (4) and (6), respectively) can be estimated. Comparison of all three methods will indicate whether FZ1 has a relatively uniform aperture, or a high degree spatial variability.

GROUNDWATER VELOCITY DETERMINATION

Hydraulic and forced-gradient tracer tests are used primarily to obtain estimates of the fracture aperture. Once the aperture and hydraulic gradient are known the groundwater velocity is readily calculated from Poiseuille's equation for laminar flow in a parallel plate opening and is given by

$$(7) \quad V = -\frac{pq}{12\mu} \frac{b^2}{dl}$$

where μ is the dynamic viscosity of water, p is the density of water, and the hydraulic gradient is taken along the flowline. Substitution for a fracture aperture of 160 μm and a hydraulic gradient of 0.01 yields a groundwater flow velocity of approximately 20 m day^{-1} through FZ1. If this value is accurate, then groundwater contamination could quickly become widespread should any contaminant enter this fracture. Of course, numerous assumptions and uncertainties linger behind this value. For example, the withdrawal well for the hydraulic test may have been located in a large-aperture zone which may not reflect the average aperture in FZ1. This would lead to an overestimation of the velocity.

The groundwater velocity calculated from equation (7), however, can be checked by two additional independent methods: borehole dilution and natural-gradient tests. The borehole dilution method provides a direct measurement of the localized velocity rather than indirect calculation by equation (7). The test involves first isolating a fracture zone by means of packers and then monitoring the time rate of change of a suitable tracer contained within the packed off interval. From the concentration history and the volume of the packed off interval, a simple mass balance equation allows calculation of the mass flux flowing through the cross section of the borehole (Drost et al., 1968). The calculated mass flux can then be compared with the value estimated from equation (7)

$$(8) \quad q = db V$$

where d is the diameter of the borehole and db is the cross sectional area for flow from the fracture into the packed off interval. The natural-gradient test calls for the release of a tracer slug followed by the monitoring of the plume as it moves through the fracture under the in situ hydraulic gradient. From such data, effective velocities could be ascertained directly. To our knowledge, no record of a successful natural-gradient tracer test in fractured rock exists in the literature. Such a test would offer a unique opportunity to evaluate the reliability of groundwater velocities predicted from in situ measurement of fracture aperture and hydraulic head. In addition, it would also allow for the monitoring of a contaminant as it moves through fracture under a natural gradient and thereby make it possible to separate out advection, dispersion, and matrix diffusion effects. Both borehole dilution and natural-gradient tracer tests are expected to be conducted at the Clarkson field site early this fall. These test will provide additional

constraints for the fracture aperture and groundwater flow velocities calculated from hydraulic and induced gradient tests.

SUMMARY

In this paper we have numerically examined potential errors in the interpretation of hydraulic and induced-gradient tracer tests that are carried out to obtain *in situ* values of fracture aperture. The volume balance aperture is not a reliable estimate because of its sensitivity to errors in the assumed geometry of the region where water is withdrawn. Large differences between hydraulic and tracer apertures are possible because of differing sensitivities to the effects of variability in fracture aperture and network geometry. To derive estimates of aperture and groundwater velocity using results of hydraulic and tracer tests, it appears that an approach is needed that provides for additional constraints on the flow field. Borehole dilution and natural-gradient tracer tests may provide direct measurements of the groundwater velocity, and thereby serve as additional checks and constraints for hydraulic or induced-gradient tracer tests.

Preliminary work at the Clarkson site yield a hydraulic aperture of 160 μm , a hydraulic gradient of 0.01, and a groundwater velocity of 20 m day $^{-1}$. Based on the encouraging results obtained from hydraulic tests of FZ1, four additional boreholes were drilled at the site in late summer 1987. The four holes were drilled equidistance from the points of the cross such that the central well, UW2, is surrounded by a square composed of eight wells. In late fall, we expect to conduct induced-gradient tracer tests to measure the *in situ* aperture and thereby provide a second estimate of the velocity in FZ1. In early 1988, borehole dilution and natural-gradient tests to measure the velocity directly are planned. Upon completion of these test, it will then be possible to assess whether the groundwater velocity determined from measurements of hydraulic head and fracture aperture correctly represents the *in situ* velocity in fracture zone FZ1. If our preliminary finding of large groundwater velocities in the Dundas shale at the Clarkson site is correct, then its is reasonable to expect that groundwater contamination could quickly become widespread should any contaminant enter the fracture zone.

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ORIGIN AND STATE OF NEAR-SURFACE FRACTURES IN THE CLAY TILLS OF SOUTHWESTERN ONTARIO

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The origin of the fractures in the weathered horizon of the soft clay tills of southwestern Ontario is from desiccation during a climatically drier period. It is not clear what the state of stress is in the upper few metres as there is contradictory evidence from various sources using various techniques. At depths below about 3 metres, the results are not ambiguous: lateral stresses are equal to or slightly higher than vertical stresses, and all data indicate that fractures are closed. However, it is the upper 2-3 metres that are critical to lateral flow in the system, and the fractures at this shallow depth seem to be open and interconnected. Also, study of clay tills at several locations indicate that a general conceptual model of macrofabric of these materials may be appropriate, but that there are variations of a site-specific nature (Vorauer, 1987).

It is difficult to decide whether fractures are open or closed based solely on conventional piezometric tests. Borehole smear and damage during piezometric installation in relatively deformable materials tends to seal off fractures (Bruce, 1987), so that the piezometer is insulated from the effects of fractures on flow. Direct observation in trenches is inadequate because of strains associated with unloading which tend to open fractures (Vorauer, 1987). Flow data from a series of constant head tests at different depths at one site suggest that fractures may be closed at depths below perhaps 3-5 m, but are likely open at shallower depths. This means that the hydraulic conductivity of the upper zone may be one or two orders of magnitude greater than the lower zone (Harding, 1986). In the lower zone, laboratory and lowest field values of hydraulic conductivity are similar, on the order of 10^{-8} cm/s. In the upper few meters, much higher values of lateral conductivity are likely to be encountered, perhaps as high as 10^{-6} cm/s.

A conceptual model for the macrofabric of SW Ontario grey/brown clay tills is presented. The diagram is schematic only, and significant site specific variations are to be expected. For instance, many sites show an undulating boundary between the oxidized and unoxidized units (3/4), and the boundary cannot usually be characterised by a sharp line, as oxidation alterations can extend to considerable depths on fracture surfaces.

Zone 1 is the congeliturbated and bioturbated zone, probably equivalent to maximum depth of penetration of ice-forming temperatures. This zone has a fabric indicative of remolding, and whether or not fractures can be found is irrelevant because of the open fabric. Organic content is high and hydraulic conductivity is several orders of magnitude higher than the deep undisturbed gray clays. Oxidation is heavy, and continues active to this day. Under most conditions, this zone is unsaturated.

Zone 2, to a depth of perhaps 3-5 metres, has vertical fractures mostly open and interconnected sufficiently so that flow is dominated by the fractures rather than the matrix. There are also some horizontal fractures, but these are much less frequent, and are probably in a closed state re-

sulting from the overburden weight. All fractures have a clearly oxidized halo around them and the clay is distinctly brown. It is suggested that the great majority of lateral flow in the system occurs in these upper two zones, and there is little mixing of any kind, except diffusive mixing, with materials in zones 4 and 5.

Zone 3 is still in the brown oxidized zone where the historical past has seen active breakdown of minute quantities of sulphides, generating the ferric oxide responsible for the brown colour verging on slightly red. However, fractures are closed in this zone to the degree that on a local scale (the scale of a piezometer) there is no evidence that flow is significantly affected by the fractures. Constant head test data show approximately linear heads for different gradients, and these values approach laboratory values. The 2/3 boundary is not abrupt, but the differences in behavior are significant.

Zone 4 is the grey clay, but with some evidence for fractures, clearly closed. Some deeper features, mainly root holes and perhaps the occasional larger fracture, do penetrate into this zone from the upper brown clay, but have only a thin brown halo which differentiates them from the surrounding grey clay. There is no evidence for lateral continuity of fractures whatsoever. The hydraulic conductivity is unaffected by fractures, and is representative of intact grey clay.

Zone 5 is below any evidence of root structures or fractures, and the clay is fully intact, the only features being those of a sedimentary nature.

There is some evidence for two types of discontinuities. The frequent, closely spaced but impersistent and low aperture fractures are by far the most common. They are easily seen and mapped on the walls of trench excavations (Vorauer, 1987). They have a brown halo adjacent to them, but significant mineralization on the surface of these fractures has not been observed. There is some evidence for the existence of larger, deeper features, likely relict tap root holes, with perhaps associated fractures extending radially for short distances. The evidence is not clear because of a limited number of access trenches to sufficient depths to permit an unambiguous data set. These features have minerals on the fracture surfaces, and have clearly been significant conduits for mass transport in the system in the geological past. The degree of lateral connectivity of these features at depth is thought to be very low, if they are interconnected at all, therefore they have no effect on lateral flow on the system.

The writer recommends that more study of the engineering geology of the fractured clay tills be undertaken to ascertain whether this model of macrofabric is adequate for generalization, or whether it is applicable only to some sites.

Engineering Recommendations

Until data to indicate otherwise is available, a conservative assumption is recommended for the condition of the fractures in the upper 5 m of the SW Ontario clay tills: we must assume that they are open and active elements in the flow regime and land fills must be designed accordingly. To assume

otherwise is dangerous, as the resulting type of error leads to unacceptable environmental risks. Being conservative carries with it a cost, but the results of an erroneous conservative assumption are environmentally acceptable.

1. Fractures in the upper 3-5 metres are assumed to be open. This implies that in order to guarantee an effective seal, these materials must be removed and recompacted, isolated using trench cutoff walls or similar systems, or improved by some other means to reduce lateral flow capacity. Vertical flow is not considered a serious issue by comparison.
2. Because of the currently unresolved issue of flow data interpretation in smeared and disturbed piezometer emplacements in soft fractured clays, hydraulic conductivity data from the field can be taken only as a lower bound: the actual values may be significantly higher. This is because in soft materials, all damage leads to lower values measured.
3. To avoid opening up closed or latent fracture systems, excavations should be kept shallow and with gentle side slopes. Deep, steep trenches tend to allow adjacent material to expand, opening fractures. This also is worthy of study using carefully placed piezometric tips.
4. Improved methods for installation of piezometer tips in fractured, relatively soft clays are required before we can develop full confidence in field-derived hydraulic conductivity measurements.
5. Cheaper methods of mitigating the effects of open fracture systems should be pursued, as these could be used to improve current landfills as well as building new sites.
6. There is evidence that the stress state and the fracture condition in the upper five meters is not clearly known, and these questions, along with their ramifications, should continue to be investigated, as they have considerable effect on fracture state which dominates the flow regime in the upper zones.
7. There is always a significant site-specific component, and study of current site investigation practice for landfill location should be given undertaken. The model presented here is conceptual and limited: it must be refined, and must be assessed quantitatively for individual sites.

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RESEARCH MANAGEMENT
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WASTE MANAGEMENT PLANNING FOR
PHARMACEUTICAL INDUSTRY, PHASE II

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Waste Management Planning for
Pharmaceutical Industry:
Phase II, Data Analysis and Assessment

The first phase of this study was presented at the 7th Technology Conference, in December, 1986(1). The present report covers progress on Phase II.

In reporting on Phase I, we noted difficulties in interpreting replies to our questionnaire, and in eliciting replies from certain firms. These have now largely been resolved, though some anomalies persist. We received waste-generation data from 35 respondents, including six hospitals. Through the courtesy of the Ministry of the Environment, we have also had access to the waste disposal data reported to the Ministry under Regulation 309 by 22 establishments, including four hospitals. Some establishments have reported data to us but not to the Ministry, and vice versa. In Table I the data from both sets are collected for comparison.

So far we have been able to identify only 13 streams, from sources, of hazardous wastes from this industry in Ontario. The nature and quantities of wastes are summarized in Table II.

Written requests were made to pharmaceutical manufacturers to provide us with lists of their products, to enable us to identify any that contain ingredients that come under Regulation 309, Schedule 2(A). This is proving to be a longer task than we anticipated as some of the manufacturers' lists were long. It involves several steps for each product listed. The trade name is correlated first with the pharmacological generic names of the active ingredients as listed in available pharmacopoeias (2) then the generic names are translated into chemical names, using the Merck Index (3) and similar sources. Finally the list of chemical names is compared to Schedules 2A and 2B. Only 10 manufacturers have responded to this request directly. We expect to be able to obtain other lists through distributors, drugstores and local medical associations. We are not ready to report on this correlation at the time of writing.

Plant visits were planned to obtain more detailed data on waste streams and costs for disposal. These have largely been cancelled, as the advice we have received is that they are unlikely to be productive. We have instead made a number of long telephone calls that have been very helpful, and have cleared up some misunderstandings, both on our part and on the part of the industry people we have talked to.

CONCLUSIONS:

Our provisional conclusions, to be confirmed in the final phase of this work, can be summarized under four headings:

- (a) Nature of the pharmaceutical industry: This industry is basically a branch of the chemical manufacturing industry, and should be treated as such. Owing to strict quality control, the wastes generated that are of specifically pharmaceutical nature are minimal. They consist of small quantities only of rejected or outdated products and intermediates. Cases such as the "Tylenol" incident, where many kilograms of a product had to be incinerated, are rare. The actual waste streams are largely composed of solvents and waste chemicals, not different in kind from those generated by other chemical manufacturers. Some have been identified as coming under Schedule 2(A) or 2(B). These are noted in Table II.
- (b) Recoverables: A number of manufacturers report potentially recoverable quantities of waste solvents. A conclusion from the telephone conversations has been that while no single plant could set up a cost effective solvent recovery system, a central or regional facility would be used. An initiative in this direction through the Pharmaceutical Manufacturers Association, perhaps with some input from the Ontario Waste Management Corporation, would be welcomed by several firms.
- (c) Landfill and Sewer disposals: It was reported (1) that we had a concern about certain substances being disposed of to municipal sewers. We can now report, as a result of interviews, that nothing identifiable as coming under Schedules 2A or 2b of Regulation 309 is currently being sent to unsecured landfill or to sewers, except in exceedingly small quantities. It is common practice for hospitals to dispose of unconsumed amounts of prescribed drugs in the regular garbage or to the drains, but the quantities are always very small. Manufacturers occasionally must dispose of small amounts of returned or off-specification products. We are assured that they are being properly handled.
- (d) Education needed: A number of manufacturers showed misunderstanding of the requirements for reporting under Regulation 309. The usual error has been over-reporting, as some have believed that they must register all the hazardous substances they use, irrespective of whether they turn up in waste streams. We recommend to the Ministry that they offer some supplementary written instructions or oral assistance to officers of companies to clarify this point.

ACKNOWLEDGEMENTS:

We wish to thank the Ministry for their generous support of this project, and for assistance in the provision of data reported to them. We are grateful also to the personnel of those manufacturers and hospitals who have taken time to respond to our inquiries.

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TABLE I

Company	Response to Questionnaire	Sent List of Pharmaceuticals	MOE Registrant	Total Weight of Waste Reported		
				on Questionnaire (kg)	on	MOE File (kg)
Adria Labo	X			5.0		
Alcon Can.			X	---		4095 (M)
Allen & Hanburys				---		---
ICI Pharma	X			8		---
ANCA				---		---
Apotex Inc.	X	X		400 ft ³		---
Astra Pharm. Can. Ltd.				400		---
Boehringer Ingelheim	X	X	X	1326.8		301 (M)
Boots Drugs	X	X		360.0		---
Bristol Labo. Can.				---		---
Canada Packers	X	X		460		---
CCG Industries Inc.				---		---
Connaught Labs. Ltd.	X		X	18,000		13,95 (M)
CooperVision Inc.				---		---
Dextan Products	X	X		190,000		---
Dow Pharm.				---		---
Eli Lilly Can. Inc.	X	X	X	1892.2	Scarborough 1/86-1/87 Aldincourt 1/86-2/87	5544.45 (M) 6760.80 (M)
Fisons Corp. Ltd.	X	X		15		---
Flint Labo. Can. Ltd.				---		---
Gleno Can. Inc.			X	---		1546 (G)
C.E. Jamieson & Co.				---		---
Cyanamid Can.				---		---
Kingsway Drug. Ltd.				---		---
Johnson & Johnson/ McNeil Consumer Prods.	X	X			J&J Inc. 4/86 J&J Baby Prods. 1/86-1/87	64242.20 (M) 13,290.75 (M)
Mead Johnson Can.				---		---
McNeil Labo. Can. Ltd.				---		---
Merrell Dow Pharm.			X	---		3071.25 (M)
Miles Pharm				---		---
Miles Labo.	X		X	18,920.3	Rexdale Concord	600 (M) 700 (M)
Hoechst-Eaton				---		---
Novo Pharm				---		---
Oregonon Can. Ltd.				---		---
Ortho Pharm.			X			7700 (M)
Parke-Davis	X	X		563.225		---
Pennwalt	X			26		---
Pfizer	X		X	540.5 75.2	London (M) 184.27 (G) London 2220 Ampthill (M) 8599.50 (G) Cornwall 4800	410 (M)
Purdue Frederick Co.				---		---
Reed & Carnick				---		---
Bristol-Meyers Can. Ltd.	X			45.7		---
Horer Can. Inc.			X	---		---
C.D. Sharle & Co. Pharm.			X	---		531.5 (M)
Smith Kline & French	X	X	X	6,649		6825 (M)
Sterling Products			X	---		18454 (M)
Syntax	X	X		226.9		---
Travenol Can. Inc.	X	X		---		348.95 (M)
Upjohn Co. of Can.	X		X	1,359		9890 (M)
U.S.Y. Can. Inc.				---		---
Venpore Ltd.	X	X		300		---
Warner-Lambert	X	X	X	---		3419 (M)
Webber Pharm.			X	---		5
Westwood Pharm.	X	X		3,900		---
Winthrop Labo				---		---
Wyeth Ltd.	X	X	X	---		38443.61 (M)

M=Manifest List

G=General List

Table II
Identified Waste Streams from Ontario Pharmaceutical Industry

Description	No. of Sources	Quantities kg.	Cost of Disposal
Biological including vaccines	4	18,500	40,000+
Controlled Drugs	1	Small	--*
Halogenated Solvents	5	--	--
Laboratory chemicals & Miscellaneous	7 (2)	200,000	15,000+
Non-halogenated solvents	5	--	--
Organic based pharmaceuticals	10	25-26000	--
Other named pharmaceuticals	7(2)	--	--
Pathological Waste	1	--	--
Radiation Hazard Waste	1	--	--
Used Oil	2	--	--

* dash means no data

** Waste streams under Regulation 309, Schedule 2A/2B are in parenthesis

MUNICIPAL SOLID WASTE
FEASIBILITY
OF
GASIFICATION
WITH

PLASMA ARC

Presented to
The Ministry of the Environment
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December 1, 1987

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BACKGROUND

Resorption Canada Limited (RCL) is a private high tech firm which was federally incorporated to design, fabricate, market and service industrial systems utilizing plasma arc technology. The Company is heavily R&D oriented since this technology is still relatively new to the Canadian industrial marketplace. Plasma arc has potential wide applicability in business and industry where a controlled source of intense heat is required.

RCL operates a plasma research facility in Ottawa, Ontario in which it conducts tests, research experiments and demonstrations utilizing a specially designed 150KW plasma arc torch. A plasma arc torch is a device for producing an electrical "flame" called a plasma which is the hottest, sustainable flame known to man. The plasma arc torch takes a very small quantity of any gas (argon, hydrogen, helium, nitrogen, oxygen, air, etc) and, using electricity, changes this gas into a plasma flame. Unlike a combustion burner flame the plasma flame can be generated in the total absence of oxygen. Heat is, therefore, generated by electrical dissociation and ionization of the gas, which can be extensively exploited in many heating applications. The arc centreline temperature can be in excess of 10,000 deg C and the arc edge temperatures can be between 3,000 and 8,000 deg C. The torch is designed and built with no moving parts for trouble free performance and easy maintenance, and it can have an electrical to thermal conversion efficiency of over 90% depending on the size of the torch. When the plasma arc torch is operated in a reactor vessel with the exclusion of oxygen the resultant processing of input materiel approaches pure pyrolysis.

Over the years a wealth of experience and knowledge has been gained with the plasma arc torch as the heat source for

the processing of a wide range of input materials. A major area of concentration has been in the processing of carbonaceous material in which pyrolysis provides for virtual complete gasification of all combustibles in the source material, while non combustibles are reduced to a virtually inert slag. The high process temperatures achieved by plasma processing ensure rapid and complete breakdown of chemical bonds and avoid the particulates and partially combusted hydrocarbons normally associated with combustion processes. Total gasification can, therefore, be achieved very efficiently and effectively. The general absence of oxygen results in significantly less air pollution from contaminants such as nitrous oxides (NO_x) and sulphur dioxide (SO₂) than is associated with conventional gasification processes.

The plasma arc processing of Municipal Solid Waste (MSW), with its high carbonaceous content, combines energy production with the destruction of a waste material with what is considered to be minimal environmental pollution. The characteristics of MSW gasification were developed a number of years ago through R&D work performed at the facilities of Plasma Energy Corporation (PEC) of Raleigh, North Carolina, with whom RCL has always been closely affiliated. The postulated 4-5 fold increase in usable output energy compared to input electrical energy represents a theoretical recovery of approximately 95% of the available energy in the input material, which together with the potential 300-350 BTU/scf product gas, the potential 20 to 1 volume reduction ratio of the silica metallic slag compared to the input MSW, and the potential minimal requirement for environmental controls are very attractive process characteristics. This becomes even more attractive when considered with the design simplicity, low capital costs and operating versatility of a plasma arc gasification

installation. However, prospective clients view these results as inconclusive since they were neither performed nor published in Canada, and there is no operational system in either Canada or the US which utilizes this technology in this application.

FEASIBILITY STUDY PROPOSAL

In an endeavour to authenticate these postulated characteristics and to increase the visibility and potential acceptability of the use of plasma technology in the gasification of MSW, RCL together with OBOE Engineering Limited of Ottawa and Ontario Hydro Research Division of Toronto submitted an unsolicited proposal to the Ontario Ministry of Energy for consideration for funding of a feasibility study. The study was to be conducted in two stages, Stage 1 to determine the higher heating value of the product gas and the total process energy balance, and Stage 2 to determine the environmental acceptability of the process and the subsequent combustion of the product gas.

Stage 1 was approved for a 1 April 1986 commencement with 49.7% of the estimated \$296K cost being funded by the Ministries of Energy and Environment. The remainder of the Stage 1 funding is being provided by the participants of the project and by Plasma Energy Corporation. Stage 2 will be reassessed for funding approval depending on the results obtained through Stage 1. The estimated cost of Stage 2 is \$190K.

All experimental work is being performed in the RCL plasma research facility. The original facility was modified in order for the required operational characteristics of such a process to be most accurately determined. The current facility is depicted at Figure 1. Modifications to the original facility included:

- a reactor vessel sized to match the power rating of the existing plasma arc torch;
- a hydraulic assisted feed system to permit continuous feed throughout the full period of an experimental run;
- a condenser to dry the product gas to determine its maximum heating value;
- a blower in the product gas line to alleviate material feed difficulties and back pressure in the reactor vessel;
- a spray process product gas cooler to remove particulates and acids, and improve the efficiency of the blower; and
- an on-line Gas Chromatograph to permit immediate readouts of the chemical composition of the product gas.

Stage 2 will require the addition of a product gas storage capability so that the gas can be stored for later use in an extended combustion test. The combustion of this gas will be conducted in the existing boiler in the RCL plasma research facility.

THE EXPERIMENTAL PROCEDURE

MSW throughput in the 150KW plasma arc facility is estimated at 400-500 pounds per hour. Each experimental run covers an eight hour period, therefore, upwards of two tons of MSW are required per run. Either shredded or "as received" city refuse can be accommodated, however, the use of shredded permits easier and more accurate ultimate and proximate analyses for comparison purposes. Steam can be introduced at varying rates, as required, to provide additional oxygen to react with the free carbon forming additional CO and H₂.

The control system is very versatile and enables one operator to process varying amounts of materiel from next to nothing to the maximum capability of the facility depending on the type of materiel being processed. The operator has continuous readout of:

- torch position within the reactor vessel;
- torch operating current and voltage;
- torch air input temperature and flow rate;
- torch coolant water input/output temperatures and flow rate;
- input materiel feed rate;
- process temperatures within and around the reactor vessel;
- gas cooler/condenser input/output gas temperatures;
- gas cooler water input/output temperatures and flow rate; and
- reactor vessel pressure.

If certain of these parameters exceeds preset tolerance levels, the torch is automatically interlocked off.

The process temperature, as monitored at the inside wall of the reactor vessel, is approximately 2000 deg F although varying temperatures are being tried in an endeavour to find the optimal temperature. The vessel is preheated to this temperature prior to the commencement of any processing. Once the operating temperature is achieved, processing commences. MSW is weighed and then placed in the feed hopper for hydraulic feed into the vessel. The hydraulic system is adjustable to permit a variable rate of input materiel to be fed into the vessel. A plunger is also available to guard against blockages. The pyrolysis operator monitors the processing rate through the temperature sensors in the vessel. An increasing temperature indicates that the vessel is emptying and a lowering temperature indicates that the MSW is being fed too rapidly. A sight window is also

available so that the material level can be visually checked whenever needed. The pyrolysis operator establishes the optimum feed rate for the process. Varying the torch input power also causes a corresponding variation in the optimum feed rate.

Output slag is permitted to accumulate in the bottom of the reactor vessel and is removed through a trap door by hydraulically tipping the entire vessel. At a 20 to 1 volume reduction ratio between the input material and the output slag a full experimental run can be conducted without the need for slag output. The slag is then removed from the vessel at the end of each run in preparation for the next run.

The volume of product gas generated is continuously recorded on a Bailey gas meter, which is calibrated prior to the commencement of any experimentation, and a continuous log of all torch operating parameters are maintained to facilitate full analyses at a later time. All other power usages through the process are also monitored together with all process temperatures to facilitate the determination of heat transfer rates and the process heat balance. The product gas chemical composition is monitored on a periodic basis with a Gas Chromatograph to ensure a good cross sectional reading of the product gas quality. The product gas is flared on exit since no further use of it is required through Stage 1. The intent through the study is to vary the operational parameters and monitor the resultant performance characteristics to determine the best operating characteristics. Figure 2 depicts the process energy balance considered achievable as derived from R&D conducted to date.

PRELIMINARY TESTING

Immediately preceding the commencement of this

feasibility study RCL conducted preliminary experimentation in the gasification of MSW for Plasma Energy Corporation. These tests were conducted in the original unmodified facility, therefore, obvious inefficiencies were present. Preliminary environmental analyses of the product gas was also conducted, as was preliminary chemical analyses of the resultant slag. The results obtained, although inconclusive due primarily to the lack of quantity of tests performed, indicated the feasibility of the process and the potential achievability of the postulated characteristics. The analyses of the resultant slag, for example, strongly supported the claim that the slag is inert and non-leachable. This level of testing, however brief, proved very beneficial at the commencement of the current feasibility study in the determination of initial process parameters.

CURRENT STUDY STATUS

We are currently nearing completion of Stage 1. Experimentation to date has been anything but routine; process changes and equipment problems have abnormally delayed the completion. Full optimization of the process remains to be achieved, however, the results are developing very much as predicted. The more fundamental of the problems which were encountered include:

- a. an excessive amount of particulate matter being carried out of the vessel by the product gas, which plugged the spray system and condenser. This volume was directly proportional to the volume/velocity of the product gas, therefore, it compounded as progress was made towards optimization. A cyclone between the vessel and the spray system largely resolved this problem; and
- b. initially, the blower operated at less than the original design throughput which repeatedly forced

product gas back through the feeder and hopper and into the lab whenever the refuse input rate was raised towards the design throughput. At this time it was not realized that the blower was faulty, therefore, the problem was alleviated by enclosing the feeder and making it and the feed hopper airtight. Subsequent rectification of the blower fault completely resolved the problem, however, findings through the problem resolution pointed out very succinctly the ramifications of any fault in the process chain which would impede the full flow of the product gas.

After full analyses of the results of the nine scheduled operational runs the Stage 1 final report will form the basis on which a decision will be made by the Ontario Ministries of Energy and Environment on whether or not to consider funding support for Stage 2.

BENEFITS/ADVANTAGES

The disposal of MSW is becoming an ever increasing problem for municipalities and environmental protection agencies alike. The standard age old disposal method of landfill is becoming increasingly less attractive as such sites are becoming full, alternate sites are becoming scarce and the knowledge and reality of contamination of adjacent facilities and property is becoming more prevalent and frightening. The alternative to landfill for MSW disposal has primarily been incineration in a number of forms. However, these forms of disposal have not been without their problems, from environmental to general public rejection on aesthetic grounds.

The success of this feasibility study to prove the postulated parameters of operation of plasma arc for the

gasification of MSW could be extremely beneficial for this application, coming at a time when new and more environmentally acceptable solutions are sorely needed. This would not only open up a complete new application field for this emerging technology but it could be a significant boon to an ever increasing number of municipalities with existing city refuse problems. This would not merely be another way to get rid of MSW, but it could be a technological breakthrough with significant benefits.

The major benefits/advantages from this process could be:

- the standard output product of the plasma arc process is a producer gas which offers considerably more flexibility for use than, for example, sites which only produce steam;
- plasma arc gasifiers can have substantially lower capital costs since they can integrate more fully into a potential owner's existing facility, as compared to sites which require integral steam boilers thereby increasing the cost of these sites by 25 to 30%;
- the output energy of the plasma arc gasifier, being a producer gas, can be stored for future use similar to natural gas, as compared to steam boiler installations where the energy is lost if it is not used virtually immediately;
- the operating temperature and the heat transfer rate of the plasma arc process can be variable, relatively at will, therefore, the optimum operating temperature and rate of reaction can be achieved, varied and maintained to minimize undesirable output pollution products and maximize the energy recovered from the input materiel;
- the plasma arc gasification process does not depend

on the combustion of any of the input materiel for the pyrolysis process, therefore, the quantity of output energy produced per unit of input materiel can be maximized;

- plasma torches have the potential to deliver the heat of reaction much faster than conventional heat sources enabling the complete breakdown of the input materiel and the production of smaller molecules which are inherently less hazardous;
- the ability to process materiel at any rate from next to nothing up to the maximum capacity of the facility and still operate at the optimal operating point is a very desirable feature;
- the fact that the materiel enters into two chemical reactions, once during the pyrolysis process for the generation of the product gas, and once during the product gas combustion process, before any by-products are exhausted to the atmosphere ensures minimization of pollutants;
- metallics and glass in the input materiel melt, thus substantially reducing the volume of the output slag and alleviating problems with its disposal; and
- there is a potential commercial market for the slag produced through plasma arc gasification of MSW thereby virtually eliminating the requirement for continued operation of controlled landfill sites for MSW.

DISADVANTAGE

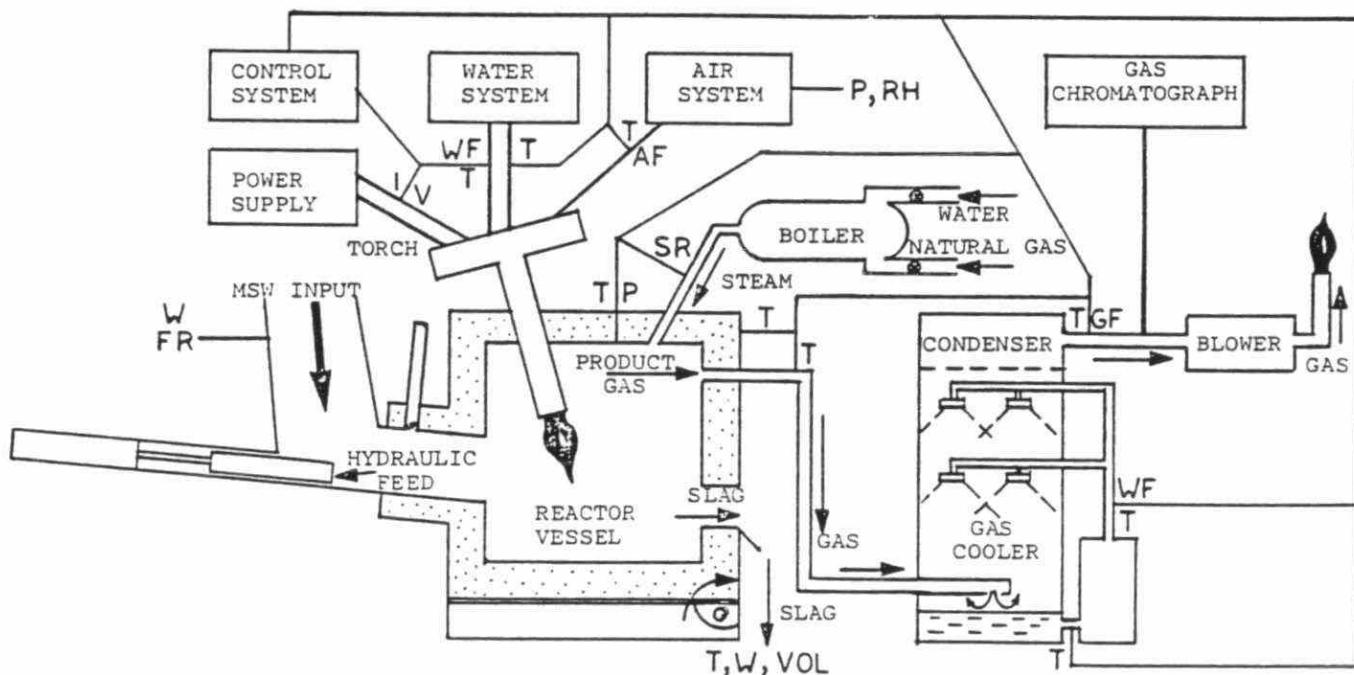
The primary disadvantage in this process is the operating costs associated with the high electrical consumption. This cost is somewhat offset by the higher volume of product gas generated and, in some cases, it can be further alleviated by operation at lower power during peak hydro usage periods. For example, demand charges can be

from 30%-90% lower, depending on the hydro district, for operation between 8PM and 8AM and all day Saturday and Sunday, which potentially can be used to advantage. The extent of this advantage would be dependent on the design and operational characteristics required of the installation.

CONCLUSION

The participants in this feasibility study remain very optimistic that the experimentation will be highly successful and the plasma gasification of Municipal Solid Waste will become a fact of the future.

FIGURE 1 - PLASMA RESEARCH FACILITY - MODIFIED



I - CURRENT (AMPS)

V - VOLTAGE (VOLTS)

T - TEMPERATURE (DEGREES C)

FR - MAT'L FEED RATE (LBS/HR)

SR - STEAM RATE (LBS/HR)

P - PRESSURE (PSIG)

AF - AIR FLOW RATE (CFM)

WF - WATER FLOW RATE (GPM)

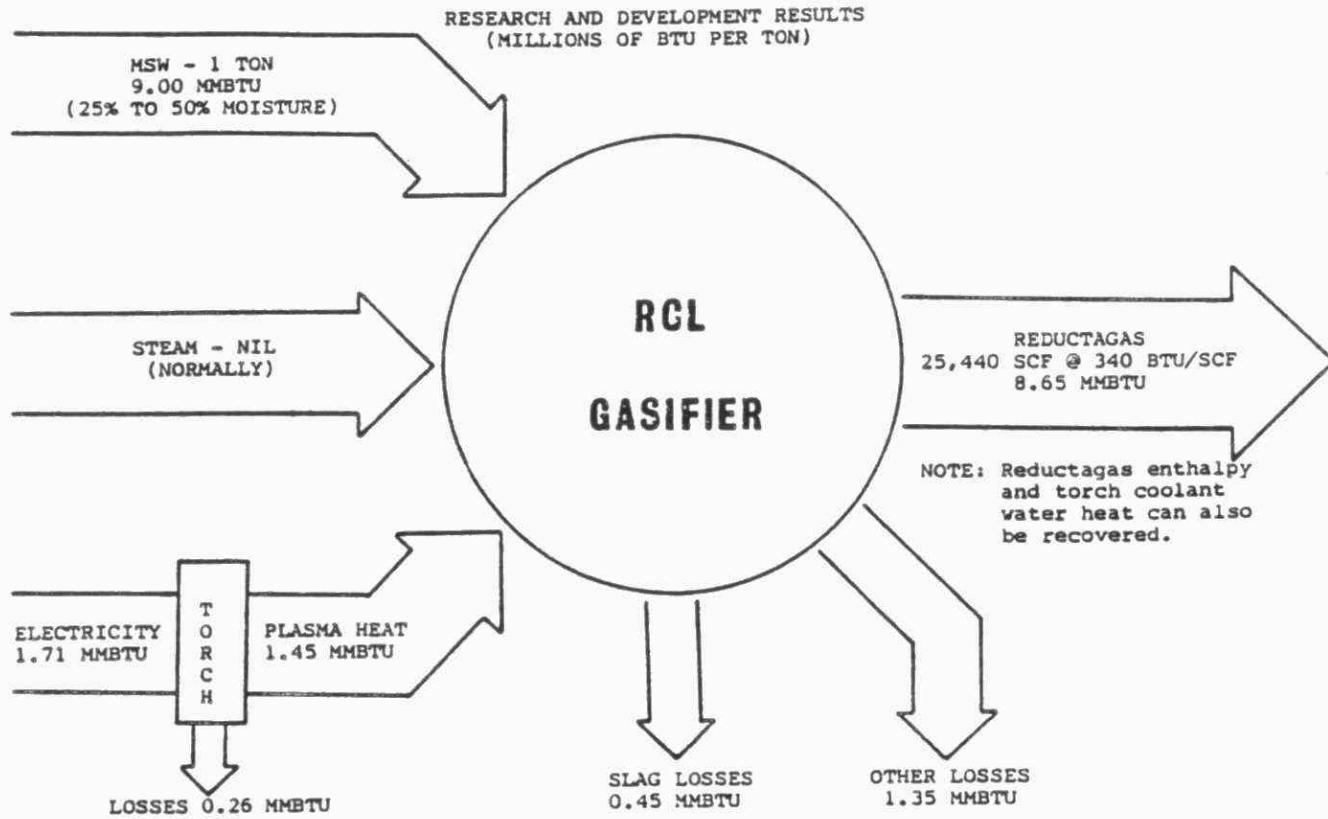
GF - GAS FLOW RATE (SCFH)

RH - RELATIVE HUMIDITY (%)

W - WEIGHT (LBS)

VOL - VOLUME (CF)

Figure 2: RESORPTION CANADA LIMITED
MUNICIPAL SOLID WASTE GASIFICATION YIELDS



DEVELOPMENT OF GUIDELINES
FOR THE UTILIZATION OF INDUSTRIAL WASTES
IN BACKFILL AND CONSTRUCTION APPLICATIONS IN ONTARIO

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ABSTRACT

The project was carried out in two phases. Phase I involved development of guidelines for the classification of industrial waste materials for backfill and construction applications, based on bulk and leachate quality analyses. The classification options developed included:

- o lakefill and shoreline disposal
- o restricted land use
- o construction use
- o immobilization

Phase II of the study involves establishing the effectiveness and reliability of the proposed guidelines through detailed bulk quality characterization and leachate testing of backfill from selected sites, as well as hydrogeologic investigations at the selected sites.

A detailed site selection process was developed to determine the four sites for detailed study. The backfill materials of particular interest were:

- o blast furnace slag
- o fly ash and/or bottom ash
- o foundry sand
- o cement kiln dust
- o sewage sludge incinerator ash

Backfill material at each site will be characterized for leachate and quality characteristics. Groundwater at each site will also be sampled and analyzed for a number of parameters.

The proposed guidelines will be modified as required, based on the results of these field investigations.

DEVELOPMENT OF GUIDELINES
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by
M. Kelleher, G. Zukovs, S. Dedhar, B. Whiffin

INTRODUCTION

Historically, selected industrial waste materials generated in Ontario such as slags, fly ash and foundry sands have been employed for backfill and in a variety of construction uses. Decisions regarding specific applications have been made on an ad hoc basis with varying amounts of supporting data. The lack of standard procedures for assessing and classifying these wastes prompted the Ontario Ministry of the Environment through its Waste Management Branch to undertake preparation of Guidelines for the Utilization of Industrial Wastes in Backfill and Construction Applications.

A tentative waste classification process was developed during Phase I of the project. In addition, waste materials produced in significant quantities in Ontario, and the uses to which these materials are traditionally employed, were identified.

A second phase program was developed to establish the effectiveness and reliability of the proposed guidelines developed in Phase I, through field studies at a number of selected sites. The site selection process was based on evaluation of known sites which were ranked on a number of criteria with high, medium and low ranking scores. Field testing will include bulk quality characterization and leachate testing of backfill samples from each of the

selected sites. Hydrogeologic investigations will also be conducted at the selected sites and will include groundwater sampling for a number of parameters.

The proposed guidelines will be modified as required, based on the results of the Phase II field investigations.

PROPOSED CLASSIFICATION PROCESS

The proposed classification process was derived from a number of Ontario Regulations in existence at the time of classification process development. Three disposal categories were recommended, namely:

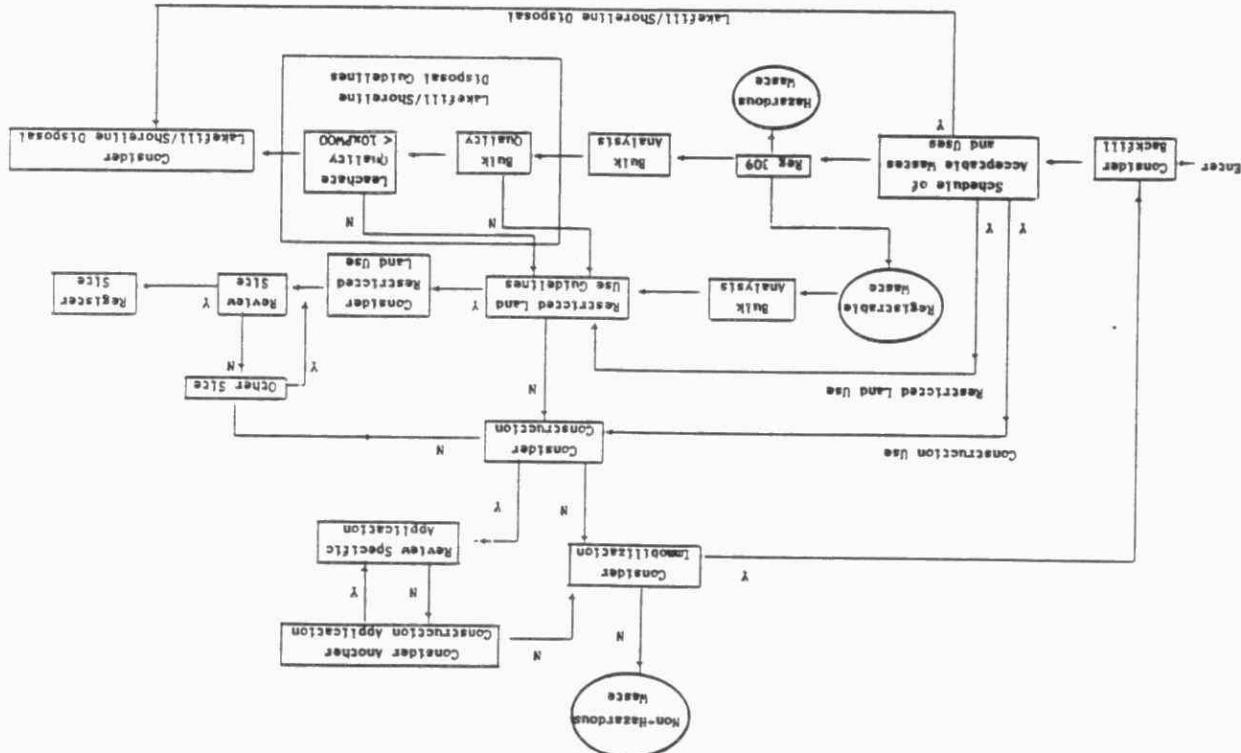
- o Lakeshore/Shoreline Disposal
- o Restricted Land Use
- o Construction Use

A fourth category, immobilization, referred to the further processing of waste material to produce a new waste material requiring re-classification. The classification of a waste material into one of the above categories would be based on results of bulk quality and leachate characterization tests.

A "Schedule of Acceptable Wastes and Uses" was also recommended in which industrial wastes would be included by common name and description, along with the use category for which the waste is considered acceptable. Wastes listed in the Schedule would not normally require bulk chemical characterization or leachate quality testing, although the MOE at its discretion may wish to review the waste use in a particular situation, and request additional testing. Waste materials not included in the Schedule would be assessed individually, by the process shown schematically in Figure 1.

FIGURE 1 - PROPOSED FLUIDIC CHART FOR THE EVALUATION OF BACKFILL AND CONSTRUCTION OPTIONS

Y - Meets the Guidelines, or is on the Schedule
N - Does not meet the Guidelines, or is not on the Schedule



CANDIDATE WASTE MATERIALS

PRODUCED IN ONTARIO

A review was carried out of waste materials produced in significant volumes in Ontario, and which would be subject to the proposed guidelines. These materials were identified as:

- o Blast furnace slag
- o Fly ash and/or bottom ash
- o Foundry sand
- o Cement kiln dust
- o Sewage sludge incinerator ash

Available information on the quantity of these materials produced in Ontario, and how they are generally used, is summarized in Table 1. A more detailed discussion of each of these materials is presented in Reference 11.

PHASE II - FIELD INVESTIGATIONS

Purpose

As part of the Phase II studies, it was determined that a field testing program would be carried out at sites containing some of the above materials. A total of four sites are to be investigated as part of the Phase II program.

Site Selection Process

An inventory of sites containing the candidate materials was developed. As no central registry of this type of information was available, the inventory was initially developed through the following sources of information:

Table 1

SUMMARY OF INFORMATION
ON SELECTED INDUSTRIAL WASTES PRODUCED IN ONTARIO

WASTE MATERIAL	ESTIMATED ANNUAL PRODUCTION (tonnes/year)	TRADITIONAL USE
Blast furnace Slag	total not available*	<ul style="list-style-type: none"> -Sold to slag handling companies for crushing, then used in road, railbed, marina, parking lot construction -At least 80% used as a granular base course aggregate for road construction and parking lots. The rest is used for other construction. An estimated 5% is used for railbed construction. -Also used for grading steel company property.
Fly Ash/Bottom Ash	1,000,000	<ul style="list-style-type: none"> -Fly ash traditionally used to fill up mined-out quarries. Also in road construction because of light weight.
Foundry Sand	626,000	<ul style="list-style-type: none"> -Some has been used to fill low lying areas in the past. Most landfilled currently.
Cement Kiln Dust	120,000	<ul style="list-style-type: none"> -Small % used in asphalt mixes. Less than 10% used in backfill applications. Most is landfilled, usually on company property.
Sewage Sludge Incinerator Ash	19,500 (Ashbridges Bay only)	<ul style="list-style-type: none"> -Six plants in Province with incinerators. -Most store as on-site in ash lagoons. -Some plants landfill the ash.

* Estimated at above 1,500,000 tonnes/year

- o Literature review to identify published information on any existing sites.
- o Discussions with members of MOE Waste Management Branch.
- o Discussions with Regional Municipalities.
- o Discussions with MOE Regional offices.
- o Discussions with environmental abatement officers at MOE District offices
- o Discussions with Federal Environmental Protection Service (EPS) staff.
- o Discussions with key industries involved, including steel companies, foundries, cement companies, Ontario Hydro, water pollution control plants, slag companies and waste disposal companies.
- o Discussions with key industry organizations, e.g. Canadian Steel Environmental Association (CSEA), Canadian Foundry Association etc.

From this extensive information gathering exercise, a list of potential sites was developed. Each site was then assessed on the basis of the criteria developed for site evaluation, presented in Table 2. Five of the ranking criteria were considered critical. These were:

(1) Information on Site Boundaries

For many of the sites, information on precise site boundaries was difficult to obtain, as extensive record keeping had not been traditionally practiced in many situations.

Table 2
EVALUATION CRITERIA FOR SELECTION OF BACKFILL STUDY SITES

	RANK		
	LOW (1)	MEDIUM (2)	HIGH (3)
GENERAL:			
- Size of potential study area	> 20 acres	5-20 acres	< 5 acres
- Distance from Toronto	> 500 km	200-500 km	0-200 km
- Info on site boundaries	none	partial info.	complete
- Existence of site specific studies (i.e. hydrogeological, waste characteristics)	none	several	many
- Existence of general area information (i.e. water well logs, geologic reports)	none	several	many
* Degree to which site represents other industrial sites or sectors	low	intermediate	high
- Proximity to recreational areas	> 5 km	1-5 km	0-1 km
- Proximity to residential areas	> 5 km	1-5 km	0-1 km
* Number of waste types backfilled at the site	> 2	2	1
- Age of site	> 10 years	5-10 years	< 5 years
* Site still in operation	no	recently closed	yes
GEOLOGICAL:			
- Soil grain size	fine	intermediate	coarse
* Complexity of stratigraphy	extreme heterogeneities	limited heterogeneities	homogeneous
- Thickness of unconsolidated deposits over Bedrock	> 30 m	5-30 m	0-5 m
HYDROGEOLOGICAL:			
- Proximity to groundwater recharge area	> 5 km	1-5 km	0-1 km
* Attenuation capacity of soils (i.e. Cation exchange capacity)	high	intermediate	low
- Potential connection to water supply aquifer	low	intermediate	high
- Hydraulic conductivity of shallow soils	> 10 cm/s	-10 - 10 cm/s	< 10 cm/s
Depth to Water Table	> 20 m	5-20 m	> 5 m
- Thickness of water table aquifer	> 30 m	5-30 m	0-5 m
SURFACE WATER:			
- Proximity to surface water bodies			
- Lakes	> 5 km	1-5 km	0-1 km
- Creeks and Streams	> 2 km	0.5-2 km	0-5 km
- Wetlands	> 2 km	0.5-2 km	0-5 km
* Key considerations			

(2) Degree to Which Site Represents Other Industrial Sites

The main objective of the programme was to study a "typical" site, so that the information could easily be applied to other similar situations.

(3) Number of Waste Types

Ideally, the study would focus on sites with one waste type only. However, if a site with one waste type only could not be found, consideration was also given to sites with two waste material types. Sites with greater than two material types received low ranking.

(4) Geological and Hydrogeological Setting

Ideally a coarse, homogeneous geological setting in a soil with low cation exchange capacity would best suit the purpose of the study, as immigration of any contaminants from the fill material to the groundwater would be unimpeded, and would be obvious in analytical results. Also, a shallow groundwater table would simplify the field program and would be an ideal situation.

(5) Operation and Age of Site

Ideally, a site which had been in operation for some time and was still in use would be most suited to the study, as a sample of the fresh material being placed could be obtained. If the site chosen was no longer in use, it was intended that a sample of the in-situ material be taken for bulk chemical characterization and leachate testing. However, this might not be representative of the quality of the material when initially placed. It was also considered desirable to

study a site which was relatively young, (less than 10 years old) in the hope that more accurate records would be maintained of the material placed.

Final Site Selection

When all the sites had been ranked on the basis of the criteria listed in Table 2, a shorter list of potential sites was developed. Each of these sites was assessed in greater detail. All available information on these sites was collected and reviewed, and each site was visited to determine any field conditions which would render it unsuitable for the purpose of the study. The four most appropriate sites were selected on the basis of this further detailed review.

On-Site Investigation

On-site investigations at each location will consist of:

- o Hydrogeologic investigations
- o Groundwater sampling and analysis
- o Backfill material sampling and analysis

Each of these tasks is discussed separately below.

Hydrogeologic Investigation

Site hydrogeologic investigations will be carried out to

- (i) Define the stratigraphy
- (ii) Characterize the hydrogeology
- (iii) Install piezometer nests in boreholes for subsequent monitoring

Four boreholes will be drilled around each of the selected sites. Drilling logs are completed in the field by a qualified geologist as drilling of boreholes proceeds, and results summarized on a standard borehole log form, to characterize the geology of each site.

Piezometers will be installed at each borehole location to facilitate monthly sampling of groundwater and water level monitoring. One of the boreholes will be located upgradient of the site in order to characterize background groundwater quality. The remaining three boreholes will be located downgradient of the site, in order to characterize the impact of backfill placement on groundwater quality.

Hydraulic testing will be carried out at each piezometer in order to characterize the hydraulic conductivity (permeability) of the hydrostratigraphic units at each site. This will be accomplished by slug tests, and augmented by pump tests, if necessary. The results of this phase of the work will define the geological stratigraphy at the site, and the direction and rate of groundwater flow.

Groundwater Sampling and Analysis

Sampling of groundwater will be conducted using a dedicated bailer suspended inside the borehole from the surface. Prior to collecting a fluid sample, a minimum of three well volumes will be removed from the well. Evacuation of the borehole fluids will continue until the clarity, pH and specific conductance of the fluids stabilize or until ten well volumes have been removed (whichever occurs first).

Borehole fluids will be analyzed for the following parameters:

- Major ions (as specified in the PDWO)
- Metals (as specified in the PDWO)
- Specific conductance
- pH
- Temperature

Specific conductance, pH and temperature will be measured at the time of sampling. Other parameters will be analyzed in the laboratory. Depending on the industrial waste of concern, testing for specific organics may be warranted. Decisions regarding organic testing will be made on a site specific basis.

It is currently proposed that the piezometers be sampled after being developed and then again in each of two subsequent months. Following completion of three months of analysis, the results will be assessed to determine if a contamination problem exists and if further monitoring is required.

Backfill Material Sampling and Analysis

Backfill material will be characterized for leachate and bulk chemical characteristics. Leachate from the backfill material will be extracted using Regulation 309 methodology, and analyzed for the following parameters:

- Major ions (as specified in the PDWO)
- Metals (as specified in the PDWO)

The backfill materials will be characterized for the parameters listed in Table 3. It is preferable that material currently being placed at each site be used for these analyses. If in-situ backfill material is necessary for leachate and bulk chemical characterization, samples will be collected during the drilling phase of the

Table 3
PARAMETERS FOR BACKFILL MATERIAL
BULK CHEMICAL CHARACTERIZATION

<u>Parameter</u>	<u>Method</u>	<u>Detection * Limits (ppm) Solids</u>
Metals: Ag	Inductively - Coupled	0.5
Al	Argon Plasma	5.0
Be	Emission Spectroscopy	0.05
Ca		5.0
Cd		1.0
Co		5.0
Cr		1.0
Cu	*The backfill material will require either an acid	1.0
Fe	digestion, fusion or leaching techniques	1.0
K		100.0
Mg		1.0
Mn		1.0
Mo		20.0
Na		100.0
Ni		5.0
P		50.0
Pb		5.0
Sr		0.1
Th		5.0
Ti		0.5
V		0.5
Zn		1.0
Zr		2.0
B		5.0
Hg	Cold Vapour A.A.	0.002
As	Hydride A.A.	0.05
Se	Hydride A.A.	0.05
Sb	Hydride A.A.	0.05
CN	Distillation & Colourimetry or Tritrimetry	0.1
Phenols	Distillation & Colourimetry	0.05
Fluorine	Specific Ion Electrode (solids require a fusion)	5.0
PCBs	Extraction, clean-up & GC/ECD	0.1

* Estimated limits based on "typical" samples. Actual detection limits may vary depending upon the nature of the samples.

hydrogeologic investigation. Bulk chemical characterization of backfill materials will be enabled through acid digestion, fusion or leaching techniques. The appropriate method will be selected based on the nature of the backfill material in question.

Data from the field investigation and laboratory testing will be summarized and analyzed, and an evaluation made as to the effectiveness and reliability of the proposed "Backfill and Construction Application Guidelines".

STUDY CONCLUSION

The proposed Guidelines will be revised as deemed necessary based on results of the Phase II work.

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SLOW RATE INFILTRATION LAND TREATMENT AND RECIRCULATION OF
LANDFILL LEACHATE IN ONTARIO

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1.0 Introduction

Slow Rate Infiltration Land Treatment

Land treatment systems are designed to circulate wastewater back into the soil-vegetation ecosystem in such a way that the maximum degree of renovation and attenuation of contaminants is achieved before the effluent re-enters the hydrologic cycle as deep drainage. The ecosystem thus acts as a "living filter" in effecting both physico-chemical and biological decontamination, with soil water recharge and plant nutrient supply being ancillary benefits.

Land treatment systems can be divided into three main types according to the mode and rate of wastewater application; slow rate infiltration, rapid rate infiltration and overland flow (Iskander, 1981; C.R.R.E.L., 1984). Each is characterized by a unique hydraulic loading rate and set of ecosystem component requirements to achieve optimum wastewater treatment. The slow rate infiltration method makes the best use of intrinsic ecosystem attenuation capacity by:

- i) maintaining an aerobic soil environment, maximizing evapotranspirational losses and minimizing deep percolation (i.e. unlike the rapid rate infiltration method)
and
- ii) by eliminating the need for recollection and possibly final polishing treatment before discharge into water courses (i.e. unlike the overland flow method).

Disposal of landfill leachate on land is not widespread in North America (Nordstedt *et al.*, 1975; Menser *et al.*, 1978). The practice is, however, widely used in the United Kingdom where the common procedure is to use specially prepared grass plots with underlying artificial tile drainage to intercept deep percolation and monitor effluent quality before discharging into surface water systems (Harrington and Maris, 1986). Landfill leachate generally contains all

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essential macro- and micronutrients and would thus seem to have a good potential for renovation through ecological systems.

Several obstacles do exist, particularly under Ontario climatic conditions, to its widespread adoption. Firstly, it is difficult for this to be a final solution when conventional land application techniques (e.g. spraying) are impracticable during the winter months (Harris, 1978). Similarly, the sizeable surplus of precipitation over potential evapotranspiration on an annual basis in this province increases the risk of excessive hydraulic loading and waterlogging in the application area, with resulting adverse effects on vegetative vigour and survival. And finally, excess concentrations of certain elements (e.g. iron) can have a significant phytotoxic effect on vegetation. If present in sufficient concentrations in the leachate, heavy metals can also accumulate in plant biomass thus precluding treatment in agricultural ecosystems (Schirado *et al.*, 1986). The phytotoxicity problem has been averted in parts of the southern United States by land treating leachate during the vegetatively dormant months of October to April (Menser, 1981).

Landfill Recirculation

Recirculation of leachate through the landfilled refuse has been recognized as a method of effecting partial leachate treatment and control of ground and surface water pollution associated with MSW landfills (Pohland, 1980; Tittlebaum, 1982). Largely pilot-scale research (Robinson and Maris, 1985; Lee *et al.*, 1986) has shown three advantages to implementing recirculation to complement a primary treatment option (e.g. land treatment, aerated lagoon). Firstly, recirculation can be used as a means of storage if the primary treatment system malfunctions or volumes temporarily exceed the system's capacity. If properly capped, the refuse will remain unsaturated and possess a large storage capacity. A subsurface application network would also allow for winter storage, since volumes would be greatly curtailed relative to the spring and fall seasons. Secondly, this practice can significantly reduce the volume of leachate to be handled by the primary treatment system through evapotranspirative losses (i.e. 30 to 35% volume reduction). And finally, recycling leachate has been shown to accelerate landfill

stabilization. By establishing a more optimum refuse moisture content, microbial activity is enhanced and a more anoxic environment is created due to increased gas evolution (Robinson and Lucas, 1985). The landfill itself thus acts as an "anaerobic filter" and substantially lowers the leachate BOD and suspended organic content. The overall result is a lower strength leachate which is likely to be more suitable for adjacent land treatment than the unrecirculated wastewater. The principal disadvantage is the increased hydraulic loading of the landfill which augments the potential for ground water contamination if the refuse cell is not double lined (Lee *et al.*, 1986). Nevertheless, by reducing the volume and strength of the leachate, landfill recirculation can be viewed as an effective "pretreatment" step, particularly if it precedes slow rate infiltration land treatment.

2.0 Study Objectives

This is a 3-year research study (1987-1990) which will yield conclusions and recommendations on specific site conditions conducive to leachate land treatment/recirculation networks. The working objectives are as follows:

1. - to evaluate slow rate infiltration land treatment of MSW leachate in forested or agricultural ecosystems using alternative land application techniques as a practicable economic, environmentally-sound and long-term solution to landfill seepage occurrences under Ontario biophysical and climatic conditions.
2. - to evaluate recirculation of leachate to the landfill surface as a partial on-site treatment method under Ontario climatic conditions.
3. - to place the technical findings of this study within the context of the land use planning for wastewater treatment and disposal.

3.0 Methodologies and Some Preliminary Results

Slow Rate Infiltration

The first year of the study has been largely devoted to experimental site selection, acquisition of the necessary approvals, design and establishment of pilot-scale installations and baseline inventories and measurements for use in subsequent monitoring of the effects of perturbation experiments in years 2 and 3 (1988-89,

1989/90). Sites selected for installation of land treatment plots and irrigation initiation in 1988 are the Essex County Sanitary Landfill No. 2 near Leamington (one unwooded installation) and the Hamilton-Wentworth Regional Landfill in Glanbrook Township (one wooded and one unwooded installation).

Each facility is to consist of three replicate blocks (randomized). Three slow rate infiltration methods will be used at three leachate application rates (i.e. 3.5, 7.0 and 14.0 mm·d⁻¹), although the irrigation program will be modified in accordance with daily ambient weather conditions (e.g. precipitation events). The experimental design includes both water-irrigated and rain-fed controls and five vegetative species will be transplanted to the plots. Spray irrigation is the treatment aimed to maximize organic contaminant volatilization and water evaporation. Trickle irrigation provides good surface distribution and optimizes use of the most active microbial soil zone (i.e. high organic matter topsoil or litter layer) in leachate renovation while eliminating direct phytotoxic follar contact with vegetation (Oron *et al.*, 1986). Subirrigation is the most aesthetically acceptable application technique in that it eliminates odour emissions and spray drift which can create a "nuisance" to local residents (Schauer, 1986). Distribution through a subsurface tile network also affords the possibility of winter application depending on local frost depth in the soil (Harris, 1978). This technique, however, does circumvent leachate rejuvenation in the microbially-active topsoil and lower subsoil temperatures may curb microbial activity despite bioactive leachate introduction.

A smaller scale version of the above experimental plot design was installed and operated at the Muskoka Lakes Landfill (District Municipality of Muskoka) in 1987. Most of the data are currently under analysis but some preliminary results with regard to vegetative stress and forest decline are presented here.

Continual spray application of leachate on the Muskoka Lakes forest understory deposits an iron-based precipitate on plant leaves to a point where the entire abaxial surface is irreversibly stained until leaf senescence in the autumn. The adaxial surface, however, remains uncoated, the leaves remain turgid and otherwise retain the outward integrity of unsprayed leaves throughout the growing season.

Spectral radiation measurements on red maple (*Acer rubrum*) leaves were made using a LI-COR model 1800 spectroradiometer. Sprayed leaves, when compared to unsprayed leaves in shaded areas, demonstrated a 4-6% decrease in reflectance and a 4-6% increase in transmittance of IR radiation (0.7 - 1.1 μm), resulting in no net increased absorbance. In unshaded areas, sprayed leaves, when compared to unsprayed leaves, showed a 6 - 8% decrease in reflectance and a 5-10% decrease in transmittance of IR radiation, resulting in a net increased absorbance of 7-15% in this waveband.

Leaf surface temperature measurements made utilising a non-contact, infrared thermometer revealed significant differences between unsprayed leaves (25.3°C) and sprayed leaves (36.0°C) in unshaded areas. A smaller but inverted temperature difference was observed between unsprayed and sprayed leaves in shaded areas (17.7°C and 16.4°C, respectively).

A LI-COR model LI-6000 portable photosynthesis system was employed to determine CO_2 gas exchange rates and stomatal conductance of sprayed and unsprayed leaves in shaded and unshaded areas. Absolute decreases in the stomatal conductance of sprayed leaves when compared to those of unsprayed leaves were observed in both shaded and unshaded areas. An investigation into photosynthetic rates has also been undertaken and additional data will be collected in a controlled greenhouse environment during the winter of 1987/88.

Landfill Recirculation

Two separate sets of cylindrical, bottom draining lysimeters have been established on the University of Guelph campus to enable the testing of two hypotheses:

- i) actual evapotranspiration of recirculated MSW leachate can be maximized to high levels on the landfill surface with vegetative cover while not seriously affecting the long-term impervious properties of the clay cap through root ramification.
- ii) the reported lessening of leachate strength (Robison and Maris, 1985) is not entirely achieved in the "anaerobic filter" (refuse body) but is largely achieved in the aerobic soil environment of the vegetated landfill cap.

All lysimeters are approximately 1 m in diameter and 1.2 m deep and all have been filled with a sequence (from top to bottom) of 50 cm of natural clay, 35 cm of MSW leachate-contaminated sand and the balance in geotextile and sand/gravel filter beds.

One assemblage of 15 such lysimeters is being vegetated with various herbaceous grass and legume (e.g. reed canarygrass, trefoil) species to simulate a clay capped landfill whose surface has been stabilized from erosive processes with these vegetation types. Leachate will be applied to accordance with evapotranspirative demand to maintain the clay material at the upper limit of plant-available moisture ("field capacity"). Water and contaminant balances conducted from the effluent draining from the lysimeters will permit assessment of the extent of leachate volume and strength reduction, respectively, after recirculation. The relative contribution made by the clay material and the various plant species to the total degree of contaminant attenuation will also be partitioned. A similar experiment will be performed on a second assemblage of 24 lysimeters but these will be planted with various woody species which have a demonstrated resistance to polluted soil conditions.

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Sampling Groundwaters for Volatile Organic Contaminants.

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EXTENDED ABSTRACT

Introduction

The determination of volatile organic concentrations in groundwater may be biased due to the loss of these organics during sample collection. This research study was designed to evaluate some of these potential sources of bias, specifically:

- (1) the volatilization of organics from groundwater entering and standing in a well or piezometer prior to sampling, and
- (2) the loss by volatilization and by sorption during groundwater sample collection.

Volatile Organic Losses From Water Entering or Standing In a Groundwater Monitoring Well.

Most protocols for sampling monitoring wells call for the removal of standing water (well flushing) with subsequent sampling of the groundwater recharging the well. Unfortunately, in low-permeability materials groundwater must still accumulate in the well for hours to days after flushing before a volume sufficient for sampling is available. During this period the groundwater is open to the atmosphere and volatilization could lower the concentrations of volatile organics.

This situation was simulated in a laboratory experiment described by McAlary and Barker (Ground Water Monitoring Rev., v. 7, no. 4, in press). The well was represented by a 1.22 m long and 5 cm diameter glass column. Sampling ports were placed at various depths and permitted groundwater samples to be collected in syringes via teflon-faced septa. The column was carefully filled with distilled water containing about 500 ug/L concentrations of the following volatile halocarbons: trichloromethane (TCM), trichloroethylene (TCEY), 1,1,1-trichloroethane (TCEA) and tetrachloroethylene (PER). The column of water was exposed to the atmosphere over its surface area at the top of the column.

Losses of volatile organics reached 10% within about 12 hours and 99% in about one month. The decay of aqueous concentrations was apparently first order with similar rates for all compounds (see Figure 1). The first order decay coefficient was $-1.27 \times 10^{-4} \text{ min}^{-1}$. Diffusion in the liquid phase was apparently fast enough so that no significant concentration gradients developed in the column.

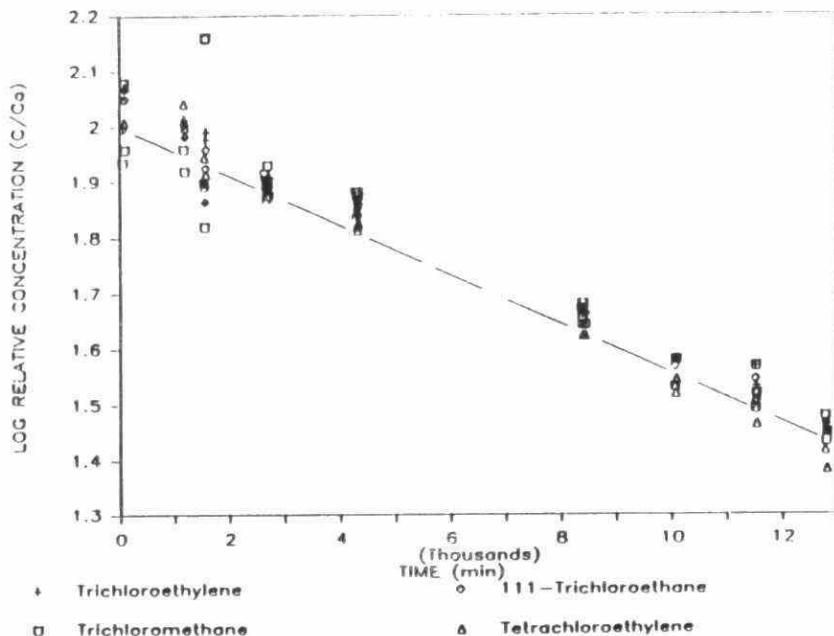


FIGURE 1. Volatilization from a standing water column.

This experiment supports the protocol requirement for removing standing water prior to sampling a monitoring well. In the context of sampling, it may be acceptable to sample a few hours after flushing a well, but, if days are required for sufficient water to accumulate, subsequent samples may be significantly depleted in volatile organics.

The problem could be even more serious when during flushing, both the well and part of the sand pack around the well screen are dewatered. Groundwater recharging the well is now also exposed to the atmosphere as it passes through the sand pack and screen. This additional exposure was shown to induce even greater loss of volatile organics in a laboratory simulation (McAlary and Barker, 1987).

Water containing volatile organics was allowed to cascade through an unsaturated sand pack and into a 5 cm diameter Teflon (R) standpipe via a 60 cm slotted interval. The standing water was then sampled. Various initial organic concentrations and recharge rates were evaluated and a number of experiments were conducted to isolate and evaluate the volatile loss by sorption onto sand and Teflon and by subsequent sampling.

The net volatile organic losses ranged from 2 to 68% for recovery periods of 5 to 70 minutes respectively. Always, more than half of this loss was attributed to volatilization.

This study demonstrates that significant volatilization losses can occur during groundwater recovery if the monitoring well is drained into the sand pack during flushing. This study also demonstrated that groundwater standing in a monitoring well can lose significant amounts of dissolved volatile organics. Therefore, such standing times should be minimized. If, in sampling low permeability materials, either or both of these problems cannot be avoided, alternate sampling protocols will be required in order to accurately determine the concentration of volatile organics in such groundwater systems.

Some Biases in Sampling Multilevel Piezometers for Volatile Organics.

Multilevel piezometers are cost-effective groundwater monitoring devices. Up to 23 narrow, Teflon or plastic tubes of varying lengths are screened over a short (<10 cm) length of their ends and attached to a PVC centre stock. This is installed through hollow stem augers which are then withdrawn, leaving the piezometer with individual tubes at various depths. This provides for detailed vertical sampling required in detailed groundwater research studies. These devices are only recommended for installation in cohesionless materials, especially sands and where vertical hydraulic gradients are minimal. Potential biases introduced in sampling such devices are reported in more detail by Barker et al. (Ground Water Monitoring Rev., v. 7, no. 2, p. 48-54, 1987).

Each tube or monitoring piezometer can be flushed and sampled using either a peristaltic pump (suction lift) or a triple-tube (gas drive) sampler. It was established that after removal of three tubing volumes, sampled groundwater had essentially constant volatile trace organic concentrations and so was deemed representative of the groundwater at that depth. Removal of three tubing volumes was, therefore, accepted as the flushing protocol.

The individual tubes could be constructed of either Teflon or polyethylene. Laboratory studies revealed that volatile trace organics such as benzene, toluene and xylenes could be sorbed onto these materials and so could introduce a negative bias in the resultant analytical data. Sorptive losses increase over time and were greater for xylenes than benzene and were greater onto polyethylene than teflon (see Figure 2). For trace organic studies, therefore, teflon is the recommended material and a short contact time between the sampled groundwater and the piezometer tubing is required.

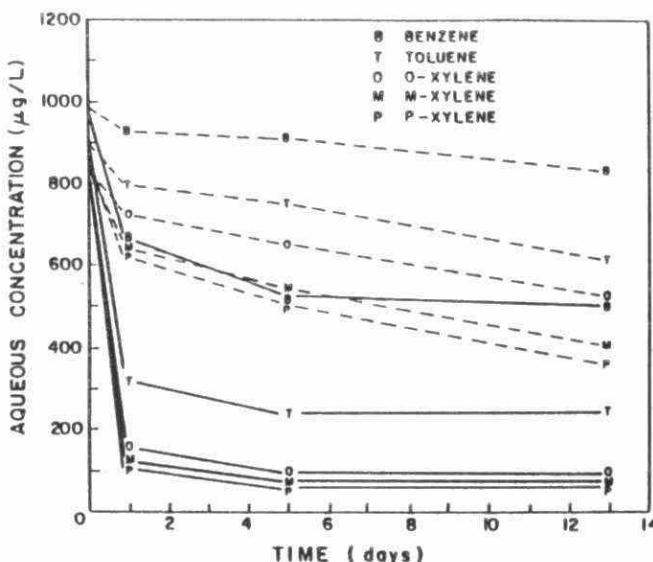


FIGURE 2. Sorption onto Teflon (---) and onto polyethylene (--) .

The possible bias introduced via volatilization during sample collection was also examined for seven volatile halocarbons in a laboratory experiment. A reservoir was sampled directly and an attached piezometer sampled with the peristaltic pump and the triple-tube sampler. The maximum negative bias was about 19% for the triple-tube sampling of the most volatile compound, 1,1-dichloroethylene. Surprisingly, the greatest bias was generally associated with the gas drive, triple tube sampler. The biases observed are unlikely to be the chief uncertainty in contaminant hydrogeological studies and are considered acceptable by the authors. Other studies suggest that this bias may be greater or smaller, may not be easily predicted and so it should be established for each monitoring situation.

Conclusions

Data for volatile organic contaminants in groundwaters may be seriously biased before and during its sampling from monitoring wells or piezometers. The major bias appears to be negative - analyses will underestimate actual in situ concentrations. Although positive bias is also possible, it is generally more easily recognized. Sampling in low permeability materials seems to be especially difficult, requiring careful well flushing followed by immediate groundwater sampling. Sampling in more permeable materials requires an appropriate flushing protocol, the use of Teflon (and probably stainless steel and PVC) monitoring devices and a sampling method that minimizes volatilization. More recent studies at Waterloo indicates that bailers, bladder pumps (Well Wizard, for example) and the newly available Waterna system are likely good choices for sampling systems.

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